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SCIENTIFIC REPORT

ABSORPTION BY CO_2 BETWEEN 6600 AND 7125 cm^{-1}

(1.4 Micron Region)

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ABSTRACT

The absorption by CO_2 in the 6600 - 7125 cm^{-1} region (near 1.4 μ) has been studied with a spectrometer having a spectral resolution of about 1 cm^{-1}. Spectra were obtained for 38 samples of CO_2 and $CO_2 + N_2$ with pressures as high as 15 atmospheres and paths as long as 933 meters. The strengths of the important bands and the half-widths of several lines have been measured. Photographs of the spectra of all the samples as well as a table of transmittance versus wavenumber are included. Also presented is a table of the integrated absorptance $\int_{\nu'}^{\nu} A(\nu)d\nu$ versus ν, with tabulations for 135 different values of ν for the largest samples.

FOREWORD

This is the second of a series of very detailed reports being published on an extensive investigation of the absorption of infrared radiation by CO_2. These reports contain photographs of spectra and extensive tables which should provide most of the information required to interpret spectra of unknown samples, such as planetary atmospheres, or to calculate the transmission through paths which cannot be simulated in the laboratory.

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SECTION 1

INTRODUCTION AND SUMMARY

Most of the absorption by CO_2 in the 6600 - 7125 cm^{-1} region (~1.4-1.5 μ) is due to the $00^{0}3$ bands of $C^{12}O_2^{16}$ and $C^{13}O_2^{16}$. A few difference bands and a combination band also absorb a small amount. The absorption in this region is so weak that it plays only a minor role in the heat balance of the atmosphere. But, because of a few rather unique features of the bands, they could be very useful in the interpretation of spectra of the atmospheres of Mars and Venus. The bands of $C^{13}O_2^{16}$ are well separated from those of $C^{12}O_2^{16}$; thus, it seems likely that the relative abundances of C^{12} and C^{13} isotopes could be determined. The difference bands $01^{1}3-01^{1}0$ are also easily distinguished from the $00^{0}3$ bands; and because of the strong temperature dependence of the strength of the difference band, quite a lot could also be learned about the temperature of a planetary atmosphere.

On the high wavenumber side of the very sharp head of the $00^{0}3$ band, is a region which is free of absorption lines, but there is considerable absorption due to the wings of lines at lower wavenumbers. Investigation of this region has provided much new information about the shapes of the wings of collision-broadened CO_2 lines. The absorption in this region is very strongly dependent on pressure and on the species of gas present with the CO_2. Quantitative absorption measurements could, therefore, be useful in analyzing planetary atmospheres.

Before spectra of planetary atmospheres can be interpreted properly, or before the absorption along any given path can be calculated, the strengths, widths and positions of most of the absorption lines must be known accurately. Courtoy[1] has measured the positions of most of the lines with very good precision; but only limited information about strengths and

widths can be obtained from his work. Howard, Burch and Williams[2] have made some quantitative measurements on the absorption in this region, but they covered a limited range of pressures and path lengths and the spectral resolution of their instrument was low.

Kuiper[3] has also investigated the absorption by large samples, but his spectra were obtained with only moderate resolution and with sample pressures of several atmospheres.

Because of the limitations of the previous work, the present investigation was undertaken for the purpose of obtaining data on samples covering wide ranges of pressure and absorber thickness and with sufficient resolution that many of the individual lines could be resolved. A long absorption cell with possible paths as great as 933 meters has enabled us to study samples of very large absorber thickness with sufficiently low pressures that the structure in the spectra is not smoothed out. A shorter absorption cell has also made it possible to study samples at pressures as great as 15 atmospheres in order to measure band strengths accurately. The mean half-width of some of the isolated lines has been measured; the half-widths of many more lines can also be determined by a careful analysis of the data.

The data are presented in great detail for the benefit of workers who require it for their analysis. Spectra of 53 samples covering a wide range of pressures and path lengths have been reproduced and digitized. The reproduced spectra are shown in Section 4 and a table of transmittance $T(\nu)$ versus wavenumber ν is presented in Section 5. Section 6 contains a table of $\int_{\nu'}^{\nu} A(\nu)d\nu$, the cumulative integrated absorptance; ν' is the smallest wavenumber considered for a given sample. Tabulations are made for as many as 135 different values of ν for the largest samples.

SECTION 2

EXPERIMENTAL METHODS

2.1 GAS SAMPLING

Samples of CO_2 and $CO_2 + N_2$ were contained in two different absorption cells which have been described previously.[4] The longer cell has a base length of approximately 30 meters and was used at as many as 32 passes, giving a total path length of 933 meters. It is approximately 0.9 meters in diameter and can be evacuated to less than 1 micron of Hg or pressurized to as much as 2.5 atmospheres. The shorter cell has a base length of approximately 1 meter and was used at as many as 32 passes. It also can be evacuated or pressurized to as much as 15 atmospheres.

The CO_2 was taken from the vapor in a dewar which contained both liquid and vapor maintained at a temperature less than about -20°C by a relief valve which never allowed the pressure to exceed 300 psig. We found that there was considerably less water in the sample if it were drawn from the vapor over the liquid rather than drawing it from the liquid and allowing it to evaporate into the cell. It appeared as though most of the water in the CO_2 container was trapped in the liquid CO_2; and if the liquid was drawn off the H_2O was allowed to enter the absorption cell. Of course the pressure, and thus the temperature, in the dewar dropped considerably and the filling rate decreased as the vapor was drawn off. When the pressure decreased to a point where the filling rate was very low, the valves were closed and the dewar was allowed to warm up before the valves were reopened. Since the large cell was filled to the higher pressures only a few times, we did not feel it was worthwhile to build a heater to submerge in the dewars to decrease the filling time. Approximately two days were required to fill the large cell to 2.5 atmospheres from two dewars of CO_2.

The cell could have been filled in much less time by drawing off the liquid CO_2 rather than the vapor, but the slower technique was chosen because of the drier samples which could be obtained. The amount of H_2O in the N_2 was much less than that in the CO_2; therefore, it was not necessary to take extreme care to reduce the amount of H_2O put into the sample with the N_2 which was drawn off as a liquid into a heat exchanger where it evaporated and entered the cell.

Before introducing a sample into the cell, it was pumped for several hours in order to get rid of most of the H_2O which was adsorbed on the walls. This can be very important, depending on the previous sample in the cell. Even after using this much care, the absorption by traces of H_2O in the sample was bothersome in some regions of the spectrum, particularly between 7000 and 7100 cm^{-1}.

CO_2 + N_2 mixtures were mixed in the cell. CO_2 was introduced to the desired pressure; N_2 was then added and the mixing was accomplished by fans inside the absorption cells. No attempt was made to change the relative abundances of the different isotopes of C or O in the samples studied. It is probably safe to assume that the natural abundances of these isotopes were present (C^{12}, 98.9%; C^{13}, 1.1%; O^{16}, 99.76%; O^{17}, 0.04%; O^{18}, 0.20%). Some results discussed in Section 3 indicate that the abundance of C^{13} was in fact about 1.1%. No check was made on the isotopes of O.

Sample pressures less than approximately 0.06 atm were measured with a U-tube oil manometer and a U-tube Hg manometer was used for pressures in the range $0.06 < P < 2$ atm. All pressures > 2 atm were measured with a bourdon-type gauge. For all except the lowest pressures used, the errors arising from the uncertainty in the pressure measurements are probably negligible.

Since CO_2 varies significantly from a perfect gas at some of the higher pressures used in this investigation, it was necessary to account for the Van der Waals' forces giving rise to the deviation from the perfect gas. In calculating the absorber thickness u, the following equation was used:

$$u = W\, p\, L\, \frac{273}{\theta}\ (\text{atm cm})_{STP}. \qquad (2\text{-}1)$$

L is the geometrical path length in centimeters,
p is the partial pressure of CO_2 in atmospheres,
θ is the sample temperature in degrees Kelvin.
$273/\theta$ accounts for the difference in density between room temperature and standard temperature, and
W is a correction term which accounts for the Van der Waals' forces and is given adequately for the pressures used in this investigation by

$$W = 1.00 + 0.0047\ p. \qquad (2\text{-}2)$$

Except for a few samples at 431°K, all measurements were made with the samples at room temperature, approximately 296°K.

In order to relate the pressure of a sample to the half-width of the absorption lines, it is necessary to account for the different broadening abilities of CO_2 and N_2 when dealing with mixtures of these two gases. Burch, Gryvnak and Williams[5] have used an equivalent pressure P_e given by

$$P_e = 1.3\ p + (P - p), \qquad (2\text{-}3)$$

where P is the total pressure. It is noted that the equivalent pressure approaches the total pressure for a very dilute mixture of CO_2 in N_2, which is a good approximation to the earth's atmosphere.

Since the simple classical theory predicts that the half-width of a line is proportional to the density of molecules, Equation (2-3) should probably be modified to account for Van der Waals' forces which cause the density to increase faster than the pressure. The adjustment can be made in the following way:

$$P_e = 1.3\ W\ p + (P - p). \qquad (2\text{-}3')$$

The factor 1.3 is not valid in all portions of the spectrum. But in a detailed study of the shapes of collision-broadened lines which will be described in a separate report,[6] we have found that 1.3 is satisfactory in regions where most of the absorption is due to lines whose centers are a few tenths of a cm^{-1} away. Therefore, it can be used near the stronger lines of most of the bands. However, the self-broadening factor should be considerably greater in a region such as that between 7100 cm^{-1} and the head of the $00^{0}3$ band at approximately 6990 cm^{-1} where the absorption is due to the wings of lines whose centers are several cm^{-1} away. The difference in the self-broadening factor arises from the fact that the shape of the extreme wings of a self-broadened line is quite different from that of a nitrogen-broadened line. Equation (2-3') probably gives a good equivalent pressure in the spectral region covered by this report, except from 6990 to 7100 cm^{-1} and from 6797 to 6810 cm^{-1}. These regions will be discussed in the report on collision-broadened lines mentioned above.

2.2 RECORDING AND CALIBRATION OF SPECTRA

The spectrometer is "home made" and is contained in a tank which could be evacuated to essentially eliminate absorption due to atmospheric gases outside of the absorption cell. The spectrometer tank, as well as another tank containing the radiation source and chopper, were connected to the absorption cell by means of flexible bellows so that all of the optical path external to the absorption cell could be evacuated.

The spectrometer is of the Ebert type with the main mirror having a 75 cm focal length. It utilized a small grating having a ruled area 64 x 64 mm with 600 lines/mm and blazed at 1.6 microns. The grating was used in the first order and a Si filter eliminated overlapping orders of shorter wavelength. A PbS cell cooled with liquid nitrogen was used as the detector. It was not necessary to cool the detector below dry ice temperature for operation in this wavelength region, but the dewar was designed to hold the liquid nitrogen for use at longer wavelengths. Cooling by liquid nitrogen was, therefore, more convenient and was used since the signal-to-noise ratio was approximately the same at both temperatures.

Three different resolution schedules were used in recording the spectra; the approximate spectral slitwidths for each schedule at three different wavenumbers are given in Table 2-1.

TABLE 2-1

RESOLUTION SCHEDULES

ν (cm^{-1})	Spectral Slitwidth (cm^{-1})		
	Schedule A	Schedule B	Schedule C
6600	0.86	1.00	1.40
6800	0.92	1.07	1.50
7000	0.98	1.14	1.60

Resolution Schedule A or B was used in obtaining most of the spectra. However, C was used for spectra of a few samples at several passes of the absorption cell for which the signal was low because of reflection losses. By increasing the slitwidth a better signal-to-noise ratio was obtained. The schedule used for each spectrum is listed in Table 4-1.

CO_2 and H_2O lines whose positions are well known, or could be calculated, were used for the wavenumber calibration of the spectra. The calibration lines are separated by an average of about 10 cm^{-1}, which is sufficiently close that the spectrum could be assumed to be linear between them. All the lines used for calibration are listed in Table 4-2 and their positions are shown on the spectra in Section 4.

Background curves were obtained with the absorption cell evacuated for each number of passes for which sample spectra were obtained. The background curve was different for different numbers of passes since the reflectivity of the mirrors in the multiple-pass optics varies with wavenumber. The appropriate background curve, which represents 100 percent transmittance, was then fitted to each spectrum and traced on it. All the sample spectra extended beyond the region of absorption on both ends of the band so that dependable "tie-points" between a spectrum and its background could be established. The transmittance was determined from the ratio of the deflection of the sample spectrum to that of the background curve at the same wavenumber.

Each spectrum was examined and compared with others as a check for consistency. Small changes were made to account for H_2O absorption. The corrections could be made reasonably accurately by comparing the spectra with those of $H_2O + N_2$ samples at the proper pathlengths and pressures. The corrected spectra were then replotted and are shown in Section 4.

As each spectrum was being replotted, pairs of values related to transmittance and wavenumber were punched on IBM cards which served as input for a computer program used to calculate transmittance and integrated absorptance as a function of wavenumber. The results of these calculations are shown in Sections 5 and 6. The instrument and the technique used in the replotting and digitizing are described in Appendix C of Reference 4.

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SECTION 3

DISCUSSION OF ABSORPTION BANDS

3.1 IDENTIFICATION AND FEATURES OF THE ABSORPTION BANDS

All of the absorption bands of the various isotopes of CO_2 which might be expected to absorb appreciably in this region are listed in Table 3-1. ν_o is the wavenumber of the center of the band for the species and transition indicated. The positions of several lines of the bands with reference "C" have been determined accurately by Courtoy.[1] The bands marked "K" were observed by Kuiper[3] in the Venus spectrum and compared with laboratory data. Values of ν_o for the bands marked SWP were determined from the energy levels given by Stull, Wyatt and Plass.[7]

Spectra of three quite different samples are shown in Figure 4-1 with the centers of the stronger bands indicated. The P-branch of the $02^{2}3\leftarrow02^{2}0$, $10^{0}3\leftarrow10^{0}0$, and $02^{0}3\leftarrow02^{0}0$ bands of $C^{12}O_2^{16}$ all overlap and are only partially resolved. The $01^{1}3\leftarrow01^{1}0$ and $00^{0}3$ bands of $C^{12}O^{16}O^{18}$ also overlap the same region. (In the notation, the lower energy level is omitted when it is $00^{0}0$.) The R-branches of all five of these bands are completely masked by the much stronger $00^{0}3$ and $01^{1}3\leftarrow01^{1}0$ bands of $C^{12}O_2^{16}$. Resolution considerably better than that used in this investigation would be required in order to positively identify very many of the lines of the five weak bands.

Although the $10^{0}3\leftarrow02^{0}0$ band of $C^{12}O_2^{16}$ should occur in a region which is free of lines of stronger CO_2 bands, we were not able to observe it. Most of the absorption near this band results from the wings of the lines of the $00^{0}3$ band. A few H_2O lines occur where one would expect to observe the R-branch; thus increasing the smallest detectable CO_2 absorption. An estimated maximum value for the strength was calculated and appears in Table 3-2.

TABLE 3-1

CO_2 BANDS BETWEEN 6600 AND 7100 cm^{-1}

ν_o cm^{-1}	Transition	Species	Reference*
6679.75	11^12	$C^{12}O_2^{16}$	K, SWP
6745.05	$01^13 \leftarrow 01^10$	$C^{13}O_2^{16}$	K, C
6780.14	00^03	$C^{13}O_2^{16}$	K, C
6884.6	$01^13 \leftarrow 01^10$	$C^{12}O^{16}O^{18}$	SWP
6897.58	$02^23 \leftarrow 02^20$	$C^{12}O_2^{16}$	SWP
6905.72	$10^03 \leftarrow 10^00$	$C^{12}O_2^{16}$	SWP
6907.09	$02^03 \leftarrow 02^00$	$C^{12}O_2^{16}$	SWP
6921.51	00^03	$C^{12}O^{16}O^{18}$	SWP
6935.05	$01^13 \leftarrow 01^10$	$C^{12}O_2^{16}$	K, C
6972.49	00^03	$C^{12}O_2^{16}$	K, C
7008.49	$10^03 \leftarrow 02^00$	$C^{12}O_2^{16}$	SWP

* K, Observed by Kuiper[3]
C, Band centers and positions of several lines measured by Courtoy[1]
SWP. Band centers calculated from energy levels given by Stull, Wyatt and Plass[7]

Some interesting features of the transmission spectra in Figure 4-1 should be noted. The difference band $01^{1}3 \leftarrow 01^{1}0$ associated with the $00^{0}3$ band of $C^{12}O_2^{16}$ is seen to be displaced to lower wavenumbers with its band head near 6950 cm^{-1}. The corresponding two bands for the C^{13} isotope appear between 6700 and 6800 cm^{-1}, the shift resulting from the heavier C isotope.

The $11^{1}2$ band near 6680 cm^{-1} has a shape quite different from that of the other bands. Its P-branch is very weak while the Q- and R-branches are relatively strong.

The spectrum of sample 22 shows two very sharp changes in transmittance at approximately 6989 cm^{-1} and 6795 cm^{-1}. These arise from the fact that the lines get progressively closer as J-values increase in the R-branch. At about J = 44 they double back, causing several lines to occur very close together with none beyond a certain wavenumber referred to as the band head. The rather strong absorption between 6989 and 7100 cm^{-1} by samples 7 and 15 is due to the strong lines whose centers occur below the band head.

Comparison of the spectra of samples 7 and 15 shows that increasing the pressure shifts the wavenumber of minimum transmittance near 6795 cm^{-1}. At relatively low pressures, the minimum in transmittance occurs very close to the band head because there are many very closely spaced lines nearby. This is true although the lines which occur a few cm^{-1} lower ($J \simeq 12\text{-}30$) are considerably stronger; but, of course, they are more widely separated. As the pressure is increased without changing the absorber thickness u, the absorption between the lines increases. (For purposes of discussion we can think of doing this by decreasing the path length.) The openings between the closely spaced lines soon become "filled-in" and the nearby absorption no longer increases with pressure. However, a much higher pressure is required to fill-in the wider openings between the stronger lines. Therefore, the absorption by them continues to increase with pressure and thus increase the absorption by them relative to the weaker lines near the band head, giving rise to a shift in the transmittance minimum.

Of course, such a shift could also be observed for the corresponding band of $C^{12}O_2^{16}$ provided the proper combination of sample parameters was chosen.

3.2 BAND STRENGTHS

The strength, or intensity, of an absorption band is given by

$$S_\nu = \int K(\nu)d\nu, \qquad (3\text{-}1)$$

TABLE 3-2

BAND STRENGTHS

Band	Species	ν_o cm^{-1}	Temperature ^oK	Portion	Strength $atm^{-1}\ cm^{-1}$ at STP cm^{-1}
00^o3	$C^{12}O_2^{16}$	6972.49	296	R-Branch	0.0205 ± 0.001
				P-Branch	0.0205 ± 0.002
				Entire Band	0.0410 ± 0.003
$01^13\text{-}01^10$	$C^{12}O_2^{16}$	6935.05	296	Entire Band[a]	0.0033
00^o3	$C^{12}O_2^{16}$	6972.49	431	R-Branch	0.020 ± 0.002
				P-Branch	0.019 ± 0.003
				Entire Band	0.039 ± 0.004
$01^13\text{-}01^10$	$C^{12}O_2^{16}$	6935.05	431	Entire Band[a]	0.0083
00^o3	$C^{13}O_2^{16}$	6780.14	296	R-Branch[b]	$22.2 \pm 1 \times 10^{-5}$
				P-Branch[b]	$22.6 \pm 2 \times 10^{-5}$
				Entire Band[b]	$44.8 \pm 2.5 \times 10^{-5}$
$01^13\text{-}01^10$	$C^{13}O_2^{16}$	6745.05	296	Entire Band[a b]	3.7×10^{-5}
11^12	$C^{12}O_2^{16}$	6679.75	296	R-Branch	$4.0 \pm 0.3 \times 10^{-5}$
				P + Q-Branch	$5.5 \pm 0.4 \times 10^{-5}$
				Entire Band	$9.5 \pm 0.6 \times 10^{-5}$
$10^o3\text{-}02^o0$	$C^{12}O_2^{16}$	7008.61	296	Entire Band	$\cdot\ 2 \times 10^{-6}$

[a] Calculated by assuming relative strengths of bands given by Equation (3-8).

[b] Based on absorber thickness u for mixture with natural abundances of isotopes (C^{12}, 98.9%; C^{13}, 1.1%; O^{16}, 99.76%; O^{17}, 0.04%; O^{18}, 0.20%). To obtain strengths of $C^{13}O_2^{16}$ bands for pure $C^{13}O_2^{16}$, multiply tabulated strength by 91.

where the integration is performed over all ν for which there is appreciable absorption. $K(\nu)$ is the absorption coefficient which is related to $T'(\nu)$, the true transmittance that would be observed with infinite resolving power, by

$$T'(\nu) = \exp\left[-u\,K(\nu)\right], \text{ or } u\,K(\nu) = -\ln T'(\nu). \tag{3-2}$$

Of course, if more than one band contributes to the absorption at a given wavenumber, $K(\nu)$, used in (3-1) must include only the portion due to the band being considered.

The strengths of the bands of interest in this report are essentially independent of pressure over the range of pressures used. However, as the pressure is increased, the widths of the lines increase until at 15 atmospheres they are greater than the spectral slitwidth used by us ($\sim 1\ cm^{-1}$). When this is the case, the observed transmittance $T(\nu) \cong T'(\nu)$, the true transmittance. Then, by combining (3-1) and (3-2), we obtain

$$S_\nu = -\frac{1}{u}\int \ln T(\nu)\,d\nu. \tag{3-3}$$

Measurements from a few different samples of CO_2 with N_2 added to a total pressure of approximately 15 atmospheres were used in Equation (3-3) to determine the strengths of the more important bands. Where possible, the samples used in any spectral region were chosen so that the absorptance was between 0.1 and 0.7. Under this restriction $A(\nu)$ was large enough to be measured reliably but not too large for $-\ln T(\nu)$ to be determined accurately. As $A(\nu)\to 1$, $T(\nu)\to 0$ and $-\ln T(\nu)$ gets very large; thus a small error in $T(\nu)$ could produce a large error in $\int \ln T(\nu)d\nu$.

It is also possible, under certain conditions, to determine band strengths from transmission spectra when the lines are much narrower than the spectral slitwidth. If $uK(\nu) \ll 1$ for all ν, $T'(\nu)$ can be expressed by the first two terms of a series formed by expanding (3-2) to get $T'(\nu) = 1 - uK(\nu)$. The true absorptance $A'(\nu) \equiv 1 - T'(\nu)$ is given by

$$A'(\nu) = u\,K(\nu). \tag{3-4}$$

It has been shown[2] that, under the usual spectroscopic conditions,

$$\int A(\nu)d\nu = \int A'(\nu)d\nu, \tag{3-5}$$

where $A(\nu)$ and $A'(\nu)$ are the observed and true absorptances, respectively. In order for Equation (3-5) to be valid, the integration must be carried out over the region containing essentially all the absorption.

Thus, we see that if $u\,K(\nu) \ll 1$, the band strength can be obtained from a measurable quantity $A(\nu)$ by

$$S_\nu = \int K(\nu)d\nu = \frac{1}{u}\int A(\nu)d\nu. \qquad (3\text{-}6)$$

The absorptance is said to be in the linear region when the conditions exist for the validity of Equation (3-6).

The major disadvantage with working in the linear region is that the absorptance is small and large errors can arise from noise in the spectrum and from slight misplacement of the background curve. The advantages are that the measurements can be made with low resolution and that the pressures need not be as high as when using larger values of $A(\nu)$ [smaller $T(\nu)$] in Equation (3-4).

Plass[8] has calculated the maximum values of $A(\nu)$ which can be used in Equation (3-6) for various band models having different line strength distributions and different ratios of line width to line spacing. He has also calculated the percentage error introduced under conditions for which the linear relationship is not quite valid. Therefore, if we have some knowledge of the widths and spacing of the lines, we can use Plass' results to determine a correction factor for a band strength calculated by the use of (3-6). This technique is frequently quite helpful when dealing with CO_2 which has reasonably regular line spacing.

For $\Sigma\leftarrow\Sigma$ fundamental or overtone bands such as $C^{12}O_2^{16}$, the strength S_m of a given line within a band is related to the strength S_ν of the entire band by

$$S_m = S_\nu\,|m|\exp\left[-\frac{B''\,m(m-1)}{k\theta}\right]\Big/ Q_r. \qquad (3\text{-}7)$$

$m = J + 1$ for the R-branch and $-J$ for the P-branch. B'' is the rotational constant of the lower state; k is Boltzmann's constant, and θ is the temperature. Q_r is the rotational partition function. Equation (3-7) is not valid for a $\Pi\leftarrow\Sigma$ band such as $11^{1}2$.

The results of the band strength measurements are summarized in Table 3-2. Since u is expressed in atm cm_{STP} according to Equation (2-1), values of band strengths are in $atm^{-1}\ cm^{-1}_{STP}\ cm^{-1}$. The STP refers to the absorber thickness but not to the temperature at which the measurements are made.

The P-branches of the $00^{0}3$ bands of both $C^{13}O_2^{16}$ and $C^{12}O_2^{16}$ are overlapped by the P- and R-branches of the difference bands. Therefore, any measurement in the region of overlapping necessarily includes the contributions of all these bands. In order to calculate the different contributions, it was assumed that the relative strengths of the bands are given by[9]

$$\frac{S_v(01^13 \leftarrow 01^10)}{S_v(00^03)} = 2 \exp(-hc\,667.4/k\theta). \qquad (3\text{-}8)$$

θ is the absolute temperature; 667.4 cm^{-1} is the difference between the energy levels 01^10 and 00^00; and h, c, and k represent the usual physical constants. The factor 2 arises from the double degeneracy of the 01^10 state. By substituting the proper values into Equation (3-8), we obtain 0.078 for 296°K, and 0.215 for 431°K, the two temperatures at which measurements were made.

The strengths of the R-branches of the 00^03 bands were measured directly since they are relatively free of lines from other bands. The P-branches of the 00^03 bands were determined by subtracting the calculated strengths of the $01^13 \leftarrow 01^10$ band from the combined strengths. It is noted that the strengths of the P- and R-branches are very nearly equal. A summation of the strengths of all the lines given by Equation (3-7) indicates that the R-branch should contribute approximately 52% and the P-branch 48%. The deviation of our measurements from this ratio is less than the uncertainty.

A comparison of the changes in transmittance at the band heads near 6990 and 6950 cm^{-1} indicates that Equation (3-8) is at least valid to within 15 or 20%. At 296°K the change in the envelope near 6950 cm^{-1} for a sample having absorber thickness u_1 and equivalent pressure P_e is approximately the same as that near 6990 cm^{-1} for a sample with the same P_e and $u_2 = 0.078\ u_1$. There are no two samples which differ in u by exactly a factor of 0.078, the theoretical ratio of the strengths of the bands. But, it is possible to estimate the change in transmittance for a given u from smooth curves through points representing different samples.

The strength of the $01^13 \leftarrow 01^10$ band of $C^{12}O_2^{16}$ is seen to increase with temperature between 296°K and 431°K with part of the increase coming at the expense of the 00^03 band. The combined strengths of these two bands are 0.0443 ± 0.002 at 296°K and 0.0473 ± 0.004 at 431°K. Because of the uncertainty in the measurements, it is not possible to determine if the increase is significant. At 431°K, the estimated error is larger than at room temperature because of reduced stability in the optics and possible error in temperature measurement which results in a corresponding error in the value of u used in the calculation.

The strength of the 00^03 band of $C^{12}O_2^{16}$ is approximately 91.5 times that of the $C^{13}O_2^{16}$ band, where the value of u used in the calculation was that of both $C^{13}O_2^{16}$ and $C^{12}O_2^{16}$ in a sample for which the abundance of the isotopes was not intentionally altered. If we assumed that the strength of the band was not altered by changing the C isotope, the relative strengths should be in proportion to their abundances, 98.9/1.1 90. Since this ratio is in good agreement with the observed ratio of 91.5, it is probably safe to assume that the isotopes in our samples were present in their natural abundances.

The R-branch of the 11^12 band is reasonably well isolated from the P- and Q-branches and its strength could be determined separately. But, because of the overlapping of the P- and Q-branches, it would be difficult to measure the individual contributions. The $10^03 \leftarrow 02^00$ band could not be detected; therefore, it was only possible to set an upper limit on its strength. It is almost certainly not more than 2×10^{-3}, and is probably quite a bit less.

3.3 HALF-WIDTHS OF ABSORPTION LINES

The shape of a collision-broadened CO_2 absorption line within a few cm^{-1} of its center can usually be represented by the Lorentz line-shape equation[10]

$$k(\nu) = \frac{S_m}{\pi} \frac{\alpha}{(\nu - \nu_o)^2 + \alpha^2}. \qquad (3\text{-}9)$$

$k(\nu)$ is the absorption coefficient of the single line; S_m is its strength, ν_o is the line center, and α is the half-width which is proportional to pressure.

Under the condition that $S_m u/2\pi\alpha \gg 1$, an absorption line is opaque within a few half-widths of its center. The line is then commonly referred to as a strong line.

Ladenberg and Reiche[11] have shown that the integrated absorptance of a strong line with Lorentz shape is given by

$$\int A(\nu)d\nu = 2\sqrt{S_m u\, \alpha} \quad \text{or} \quad \alpha = \frac{\left[\int A(\nu)d\nu\right]^2}{4\, S_m\, u}, \qquad (3\text{-}10)$$

where the integration is carried out over all wavenumbers where there is appreciable absorption. If the conditions for a strong line of known strength are satisfied, α can be determined by Equation (3-10) from a spectrum in which the line is resolved. If the conditions are not satisfied, $\int A(\nu)d\nu$ will show a less-than-square root dependence on pressure.

Lines P2 to P20 (J2 - J20 in the P-branch) of the 00^03 band of $C^{12}O_2^{16}$ occur in a region which is free of lines of other bands. It can be seen from the spectra of a few samples at pressures less than 1 atm, that there is but little overlapping of these lines. The finite slitwidth of the spectrometer causes the spectra to appear as if there is more overlapping than there really is. If we assume that overlapping is negligible, the integrated absorptance $\int A(\nu)d\nu$ over the region containing these lines can be treated as the sum of the integrated absorptances

of all the lines. Then by using values of S_m calculated by use of Equation (3-7), we can determine α by Equation (3-10) from some of our data on samples at relatively long paths and low pressures for which the strong line condition is satisfied.

It is also possible to determine the mean half-width of several adjacent lines from $\int A(\nu)d\nu$ over the interval in which the lines occur. Values of $\int A(\nu)d\nu$ for samples 18, 19, 32 and 34 over the region containing lines P6 to P20 (m = -6 to -20) were used to calculate $\bar{\alpha}^o$, a mean half-width of self-broadened CO_2 at a pressure of 1 atm. (The superscript is used with α, p and $k(\nu)$ to denote a pressure of 1 atm.) The calculations were made by the use of the following equation which can be derived on the basis of the preceding discussion.

$$\bar{\alpha}^o = \frac{p^o}{4\,u\,p}\left[\int A(\nu)d\nu \Big/ \sum_{m=-6}^{-20} (S_m)^{1/2}\right]^2. \qquad (3\text{-}11)$$

Plass'[8] calculated results on the validity of strong-line and non-overlapping approximations were then used to calculate a correction factor for the value determined by Equation (3-11) from each sample. The correction factors depend on the parameters $Su/2\pi\alpha$ and $2\pi\alpha/d$, where d is the line spacing.

After applying the correction factors, which did not exceed a few percent for any of the four samples used, we arrived at $\bar{\alpha}^o = 0.100$ for the P6 to P20 lines. The four values obtained from the different samples deviated from the mean by less than $\pm$ 3%, but the uncertainty is probably greater than this. At best, the accuracy of the half-widths cannot be better than the values of strengths used in the calculations.

On the basis of Equation (2-3), we can conclude that the mean half-width of these lines broadened to 1 atm with N_2 would be $0.100/1.3 = 0.077$ cm^{-1}.

The P2 and P4 lines were omitted from the calculation since their strengths are so much less than the others that they could not be considered strong lines for the samples used. The lines beyond P20 were not used since they are overlapped by the $01^13\text{-}01^10$ band, and the R-branch was omitted because of considerable overlapping and less regular spacing. The data could be used to determine half-widths of lines in these regions, but more sophisticated techniques would be required.

In making the calculations, the integrated absorptance was taken over the interval between 6952.2 and 6968.4 cm^{-1}. The first point is midway between P20 and P22 and the latter is midway between P4 and P6. For the samples used, this integral is very nearly the contribution of the

lines whose centers occur within the interval. The contribution of the wings of lines outside the interval is small and is partially cancelled by the contribution of the wings of the lines within the interval which is lost.

The integrated absorptances over small intervals bounded by points midway between adjacent lines were used in Equation (3-10) to calculate the half-widths of each of the lines individually. Because of the narrowness of the intervals measured, one would expect some "scatter" in the values calculated for the different lines. For example, the values of $\bar{\alpha}^o$ determined from sample 19 varied between 0.098 and 0.111, and no significant change with J-value could be observed.

Benedict[10] has found that the half-widths of CO_2 lines in the 15 μ region measured by Madden[12] can be fitted by the following empirical equation.

$$\bar{\alpha}^o_m = 0.050 + 0.12 \exp\left[-0.16\,|m|\right] + 0.0042\,|m| \exp\left[-\frac{B''\,m(m-1)}{k\theta}\right]. \tag{3-12}$$

This equation gives 0.119 cm^{-1} for P6 and 0.093 cm^{-1} for P20 with the values for the intermediate lines falling between these extremes. A mean value of 0.103 was obtained by inserting half-widths from Equation (3-12) into the following equation

$$\bar{\alpha}^o = \left[\frac{\Sigma\, S_m^{1/2}\, \alpha_m^{1/2}}{\Sigma\, S_m^{1/2}}\right]^2 \tag{3-13}$$

The summation was made over m = -6 to m = -20 (P6 to P20).

The mean value of 0.103 based on Equations (3-12) and (3-13) is in good agreement with our 0.100; the uncertainty in line strengths alone could easily account for this discrepancy. Spectra obtained with better resolution would be required in order to determine if there is any significant variation in $\bar{\alpha}^o$ with J-value.

3.4 ABSORPTION BETWEEN 6990 and 7100 cm^{-1}

It is well known that the absorption coefficient $k(\nu)$ of a single collision-broadened absorption line is proportional to pressure at any point more than a few half-widths from the line center. (For a discussion of collision-broadened lines see references 6, 8 or 13.) Therefore, we would expect the absorption coefficient between about

6990 and 7100 cm^{-1} to be proportional to pressure, since the absorption is due to the sum of wing contributions of several lines. We have demonstrated that this proportional relationship is true, as will be seen below.

For a sample of pure CO_2, where there is self-broadening only, the absorption coefficient is given by

$$K_s(\nu) = K_s^o(\nu)\ p/p^o, \tag{3-14}$$

where the subscript s refers to self-broadening and the superscript o indicates a pressure of 1 atm.

Since there are no absorption lines of significance in this region, the transmittance would not change appreciably over one spectral slitwidth; therefore, we can assume that $T(\nu)$ the transmittance observed with a finite slit is very close to the true transmittance $T'(\nu)$. We can therefore, determine $K(\nu)$ from Equation (3-2).

By combining Equations (3-2) and (3-14), we get, for a pure CO_2 sample,

$$K_s^o(\nu) = -\frac{p^o}{up}\ \ln\ T(\nu). \tag{3-15}$$

In the case of a mixture of CO_2 plus a non-absorbing foreign gas with partial pressure p_f, the absorption coefficient is given by the sum of the contributions of the foreign gas and the CO_2,

$$K(\nu) = K_s(\nu) + K_f(\nu). \tag{3-16}$$

Since K_f is proportional to p_f, Equation (3-15) can be rewritten as

$$-\frac{1}{u}\ln\ T(\nu) = K_s^o(\nu)\ p/p^o + K_f^o(\nu)\ p_f/p^o. \tag{3-17}$$

From curves of transmittance of pure CO_2 samples covering wide ranges of pressure and path length, we have determined $K_s^o(\nu)$ for the region from about 6991 to 7100 cm^{-1}. Because of the finite slitwidth of the spectrometer (about 1 cm^{-1}) and possible errors as large as $\pm$ 0.5 cm^{-1} in calibration, we were not able to get accurate values between 6991 cm^{-1} and the band head at 6988.5 cm^{-1}. In this narrow interval $K_s^o(\nu)$ changes so rapidly that it cannot be considered constant over a slit width, and small errors in calibration also result in large errors in the calculated values of $K_s^o(\nu)$.

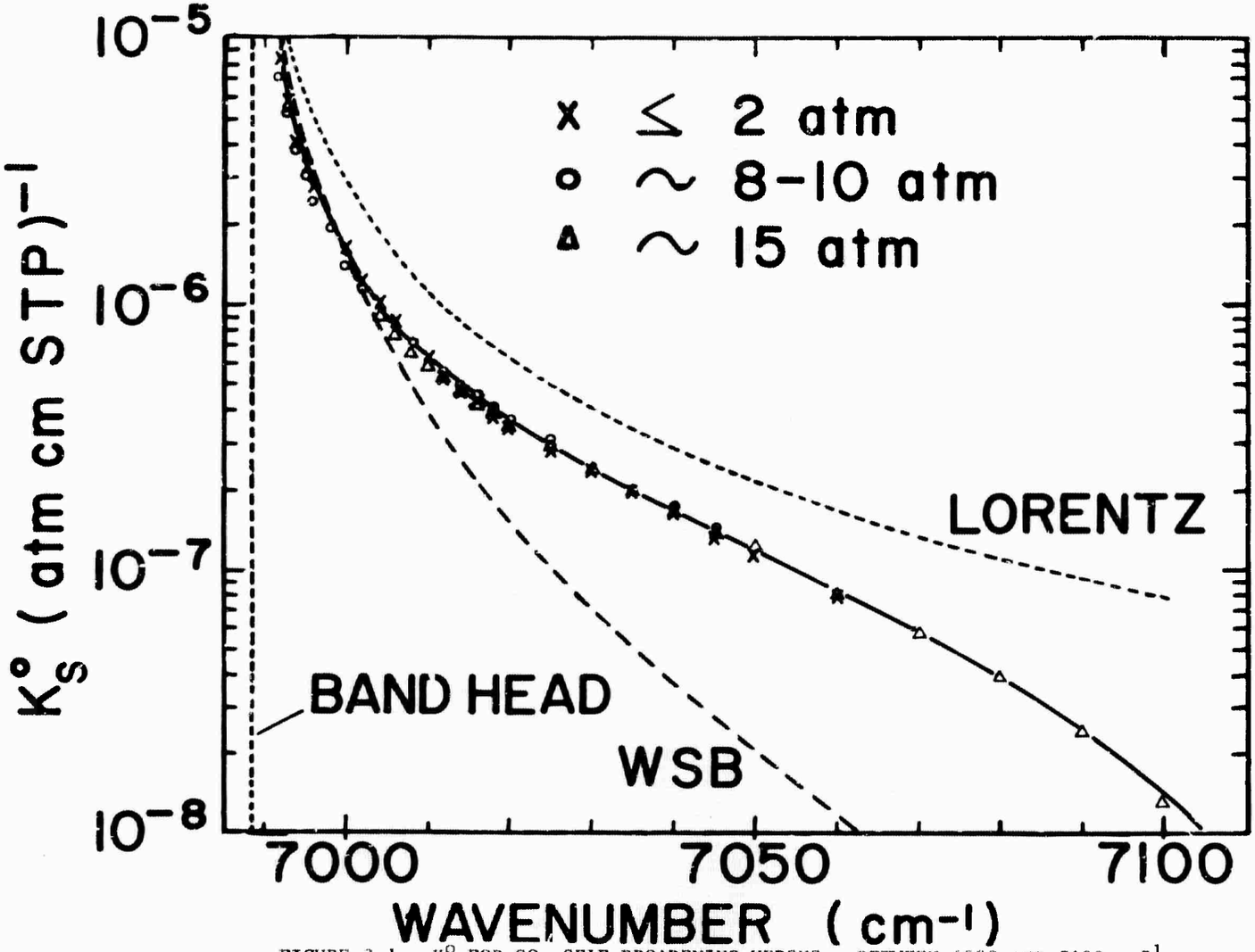


FIGURE 3-1 K_s^o FOR CO_2 SELF-BROADENING VERSUS ν BETWEEN 6990 AND 7100 cm^{-1}.

The various geometrical figures on the solid curve correspond to samples having different total pressures. K_s, the absorption coefficient for self-broadening at pressure p atmospheres, can be found by multiplying K_s^o from the figure by p. The curve marked "Lorentz" would be obtained if the lines had a Lorentz shape. The curve marked WSB would be obtained if the lines had the shape found by Winters, Silverman and Benedict[10] for the lines in the 4.3 μ band.

Figure 3-1 shows a plot of $K_s^o(\nu)$ versus ν for the region above the band head. The various geometrical figures correspond to samples having different total pressures. Since they all fall on the same curve, we can conclude that the absorption coefficient is, as we assumed, proportional to pressure.

Also shown in Figure 3-1 are two curves of calculated absorption coefficient. The one marked "Lorentz" was obtained by assuming all the absorption lines had the Lorentz shape while the curve marked "WSB" was obtained by using the line shape found by Winters, Silverman, and Benedict[10] for the lines of the 4.3 μ band. In order to perform the calculations we used line strengths given by Equation (3-7) from the value of band strength given in Table 3-2. Half-widths given by Equation (3-12) were used.

It is apparent that the lines of the 00^o3 band are sub-Lorentzian in the wings: that is, they absorb less than a Lorentz shaped line with the same half-width. However, they absorb considerably more than do those in the 4.3 μ band.

After having found $K_s^o(\nu)$ we were able to determine $K^o(\nu)$ by Equation (3-17) for He and N_2 from samples of CO_2 mixed with each of these gases. The results are shown in Figure 3-2 where a portion of the curve for pure CO_2 is included for comparison. Since it is not possible to obtain as large a value of u in a mixture as in a pure gas, and since the broadening abilities of N_2 and He are much less than that of CO_2, we were only able to measure $K^o(\nu)$ for N_2 and He over the region shown.

It is apparent that quite a lot could be learned about the shapes of the wings of collision-broadened CO_2 lines from the measurements beyond the band head. We have carried out quite an extensive set of measurements such as those described above for several different broadening gases in three different spectral regions; near 2400 cm^{-1}, near 3800 cm^{-1} and the one shown here. From these measurements we have gained considerable new information about line shapes. The results of this investigation will appear in a separate report[6] within the next few weeks.

Comparison of the spectra of samples 7 and 15 in Figure 4-1 shows that increasing the pressure has the effect of shifting the 00^o3 band of $C^{12}O_2^{16}$. In the region above the band head the absorption is a function of the product pu as can be seen by Equation (3-15). Therefore, sample 7 absorbs more than sample 15, although the latter has the larger value of u. But, between 6800 and 6900 cm^{-1}, the absorption is due primarily to lines whose centers are nearby, rather than by the extreme wings of lines. This results in a strong dependence on u and a weak dependence on p, particularly for pressures high enough that the widths of the lines are not small relative to their spacings. Therefore, sample 15 absorbs more in this region than does sample 7. Thus, the apparent shift is due to a difference in the effect of pressure in the different regions of the band, and not to a shift in line centers.

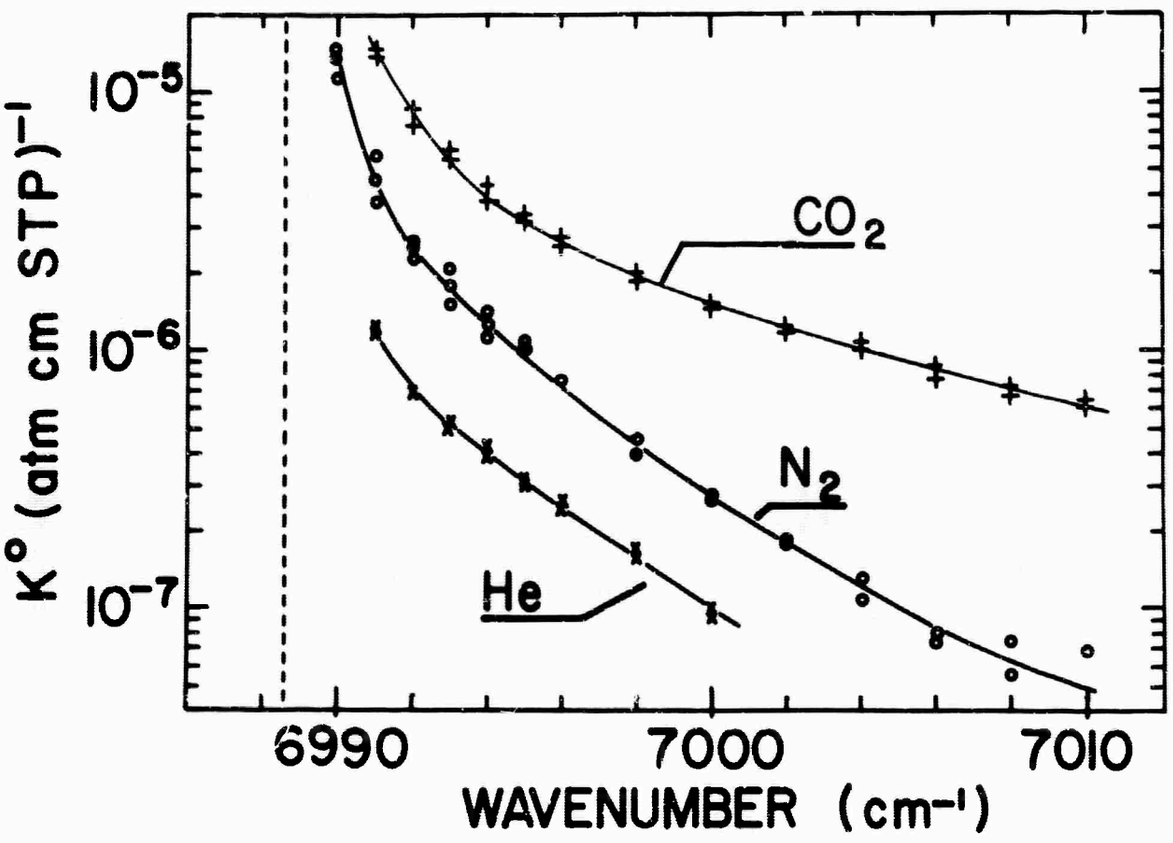


FIGURE 3-2 K° VERSUS ν BETWEEN 6990 AND 7010 cm^{-1} FOR BROADENING BY CO_2, N_2 AND He.

SECTION 4

SAMPLE PARAMETERS AND TRANSMISSION SPECTRA

4.1 SAMPLE PARAMETERS

The parameters for the 38 samples used in this investigation are summarized in Table 4-1. The following pressures are expressed in both atmospheres and torr (mm Hg):

- p partial pressure of CO_2
- P total pressure due to CO_2 and N_2
- P_e the equivalent pressure which accounts for the difference between self-broadening and foreign broadening by nitrogen. It is given by $P_e = 1.3\ W\ p + (P - p)$ where W is a Van der Waals correction given by Equation (2-2).

Also included in the table are the values of path length and absorber thickness given by Equation (2-1). The resolution schedule corresponds to the spectral slitwidth of the spectrometer used to record the spectrum. Each schedule is related to slitwidth according to Table 2-1. Replotted spectra are shown in the pages indicated in the last two columns. All samples were at 296°K, with the exception of 37 and 38 which were at 431°K.

TABLE 4-1

SAMPLE PARAMETERS

Sam. No.	p	P	P_e	p	P	P_e
	torr	torr	torr	atm	atm	atm
1	1900	1900	2500	2.50	2.50	3.29
2	1920	1920	2520	2.53	2.53	3.32
3	1920	1920	2520	2.53	2.53	3.32
4	1900	1900	2500	2.50	2.50	3.29
5	760	760	992	1.00	1.00	1.31
6	760	760	992	1.00	1.00	1.31
7	11,100	11,100	15,500	14.6	14.6	20.3
8	11,100	11,100	15,500	14.6	14.6	20.3
9	7600	7600	10,300	10.0	10.0	13.6
10	7600	7600	10,300	10.0	10.0	13.6
11	7600	7600	10,300	10.0	10.0	13.6
12	7600	7600	10,300	10.0	10.0	13.6
13	6080	6080	8200	8.00	8.00	10.8
14	3020	11,100	12,100	4.00	14.6	15.9
15	1522	1522	1995	2.00	2.00	2.62
16	6080	11,100	13,200	8.00	14.6	17.4
17	175	707	760	0.230	0.930	1.00
18	175	175	228	0.230	0.230	0.300
19	88	88	114	0.116	0.116	0.150
20	29.4	29.4	38.2	0.0387	0.0387	0.050
21	58.5	212	230	0.0770	0.279	0.303
22	58.5	58.5	76.1	0.0770	0.0770	0.100
23	1520	1520	1990	2.00	2.00	2.62
24	1520	1520	1990	2.00	2.00	2.62
25	17.8	223	228	0.0234	0.293	0.300
26	17.8	72	77.2	0.0234	0.0947	0.102
27	17.8	17.8	23.1	0.0234	0.0234	0.0304
28	8.95	8.95	11.6	0.0118	0.0118	0.0153
29	760	11,100	2025	1.00	14.6	2.67
30	506	9800	9955	0.666	12.9	13.1
31	165	9800	9850	0.217	12.9	13.0
32	506	506	660	0.666	0.666	0.868
33	165	710	760	0.217	0.934	1.00
34	165	165	215	0.217	0.217	0.283
35	5.8	21	22.7	0.0076	0.0276	0.0299
36	5.8	5.8	7.54	0.0076	0.0076	0.0099
*37	6080	6080	8200	8.00	8.00	10.8
*38	1535	1535	2010	2.02	2.02	2.65

*Samples 37 and 38 were at a temperature of 431°K; all others at 296°K.

TABLE 4-1

(continued)

Sam. No.	L Path meters	u atm cm STP	Res. Sch.	Pages on which spectra appear	
				6600-6800 cm^{-1}	6800-7100 cm^{-1}
1	933	217,000	B	4-7	4-12
2	469	110,000	B	4-7	
3	237	55,700	B	4-8	4-12
4	121	28,000	B	4-8	4-11
5	933	86,200	B	4-7	
6	237	21,900	B	4-7	4-12
7	32.9	47,300	B	4-5	4-6
8	8.26	11,900	A		4-11
9	32.9	31,700	B	4-8	4-12
10	16.5	15,900	B	4-8	4-11
11	8.26	7,930	B		4-10
12	4.16	3,990	B		4-12
13	32.9	25,100	A		4-12
14	32.9	12,200	A		4-10
15	469	87,100	A	4-6	4-6
16	32.9	25,100	A	4-7	
17	469	9,940	B	4-8	4-9
18	469	9,940	B	4-8	4-11
19	933	9,940	B		4-12
20	933	3,320	C		4-12
21	469	3,320	B		4-10
22	469	3,320	B	4-6	4-6
23	32.9	6,100	A		4-10
24	8.26	1,530	A		4-11
25	469	1,010	B		4-12
26	469	1,010	B		4-10
27	469	1,010	B		4-9
28	933	1,010	C		4-10
29	4.16	384	A		4-11
30	16.5	1,010	B		4-11
31	16.5	330	B		4-11
32	16.5	1,010	B		4-10
33	16.5	330	B		4-11
34	16.5	330	B		4-12
35	469	329	B		4-10
36	469	329	B		4-12
*37	4.16	2,170	A		4-12
*38	8.26	1,050	A		4-9

4.2 CALIBRATION AND TRANSMISSION SPECTRA

Reproductions of the replotted spectra are shown on pages 4-6 to 4-12. Except for Figure 4-1, which includes the entire spectral region covered in this report, the spectra are divided into two intervals and shown separately. The 6600 to 6800 cm^{-1} interval is shown on pages 4-7 and 4-8, and the 6800 to 7100 cm^{-1} interval on pages 4-9 to 4-12. The numbers enclosed in rectangles correspond to the sample numbers given in Table 4-1.

In most cases two or three spectra are included in a single panel of each figure in order to conserve space. The selection of the spectra for any given panel was based on how well they would fit together: no attempt was made to put them in any particular order.

In reducing the data, calibration points were taken at intervals which were short compared to the period of a small periodic error in the screw used to rotate the grating of the spectrometer. Therefore, it can be assumed that the spectra are linear between calibration points. Any error in the determination of the position of a line which might result from this assumption would probably be less than $\pm$ 0.2 cm^{-1}. The positions of known H_2O and CO_2 calibration lines used for calibration are given in Table 4-2. The H_2O lines appeared in the original spectra of some of the large CO_2 samples because of the H_2O which was present as an impurity. The CO_2 lines used for calibration are designated in the upper panels of the spectra on pages 4-7 and 4-9. The numbers on the spectra correspond to the calibration line number.

TABLE 4-2

CALIBRATION TABLE

Line No.	ν cm^{-1}	Line No.	ν cm^{-1}
1	7117.5 H*	16	6834.1 H
2	7071.0 H	17	6804.3 H
3	7045.5 H	18	6777.6
4	7021.8 H	19	6773.4
5	6978.7	20	6765.5
6	6965.7	21	6756.5
7	6959.9	22	6749.0
8	6953.4	23	6740.9
9	6946.2	24	6732.1
10	6938.4	25	6722.7
11	6929.9	26	6709.2
12	6923.9	27	6688.7 R12*
13	6917.6	28	6682.0 R2
14	6907.5	29	6669.5 P12
15	6871.2 H	30	6659.6 P22
		31	6648.3 P32

*The wavenumbers designated with an H are those of H_2O lines given by Mohler.[14] Wavenumbers of lines 27-31 were calculated by us from information given by Courtoy[1] on rotational constants. The numbers adjacent to the wavenumbers of these lines refers to the line in 11^12 band of $C^{12}O_2^{16}$. For example, R12 corresponds to the line in the R-branch which arises from a transition from the J = 12 state. All other lines are from Courtoy.

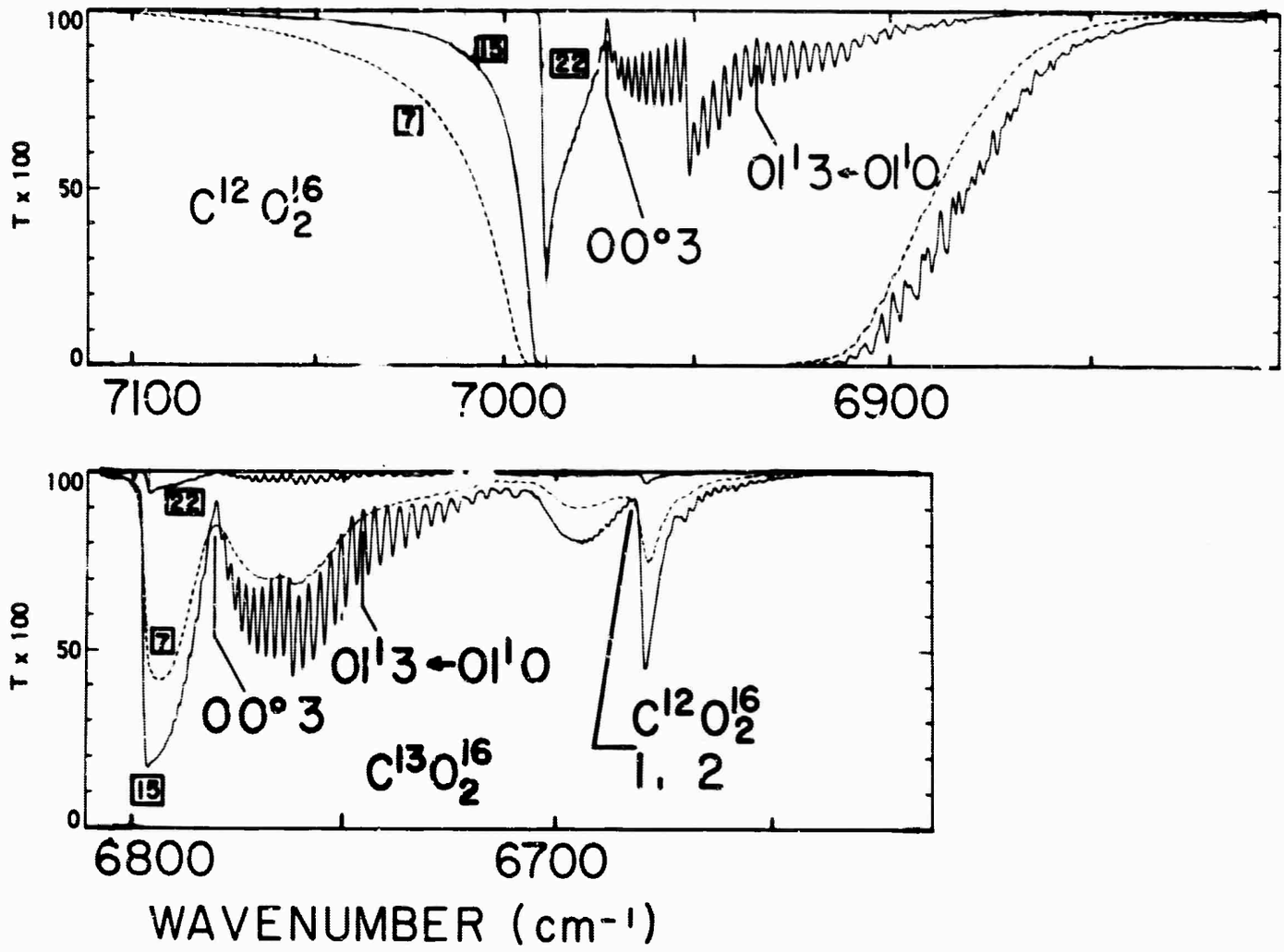
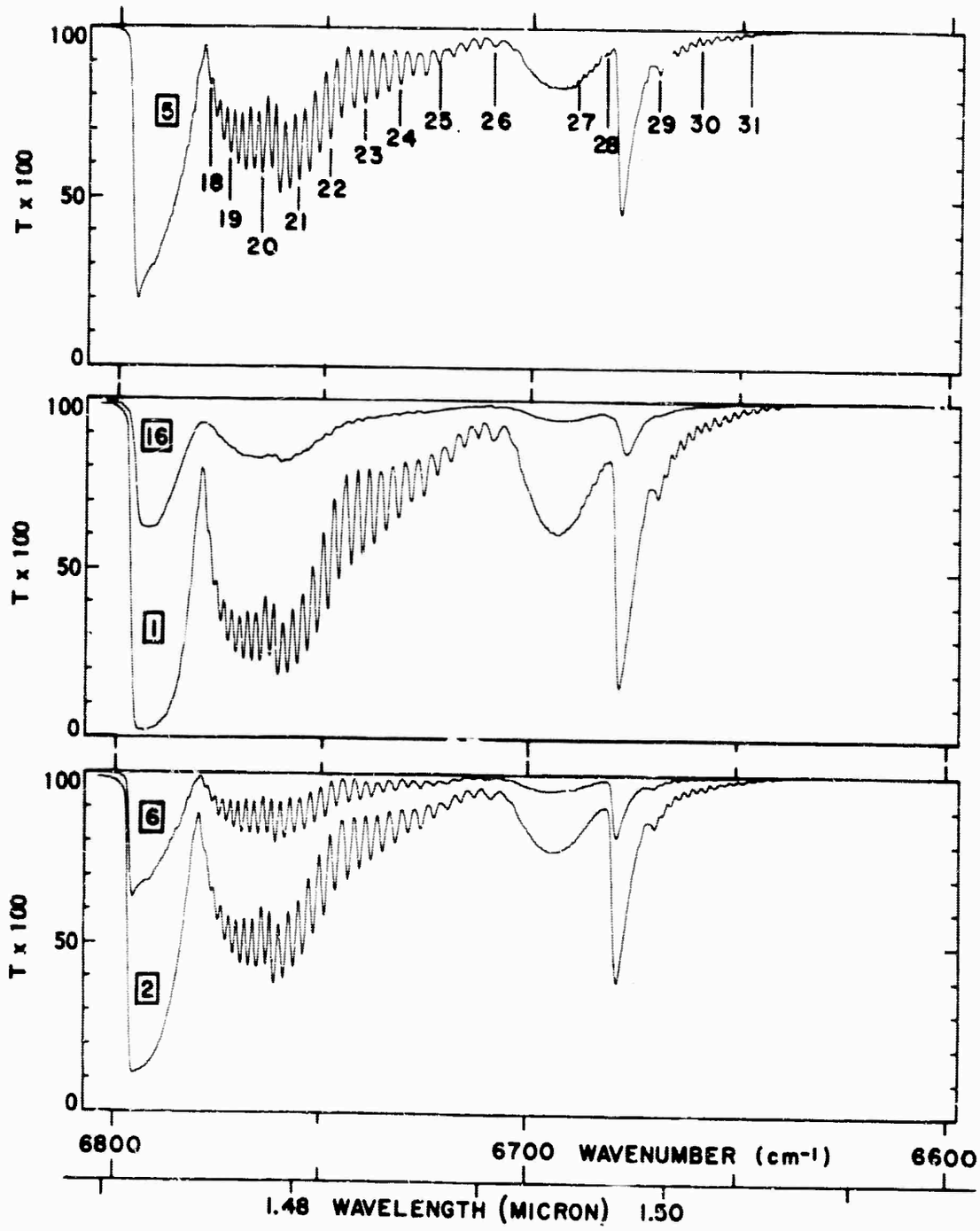


FIGURE 4-1 REPRESENTATIVE SPECTRA OF THE 6600 - 7100 cm^{-1} REGION.

The positions of the centers of the stronger bands are indicated. Other bands in this region are listed in Table 3-1 The numbers enclosed in rectangles are sample numbers. The parameters for all the samples are listed in Table 4-1.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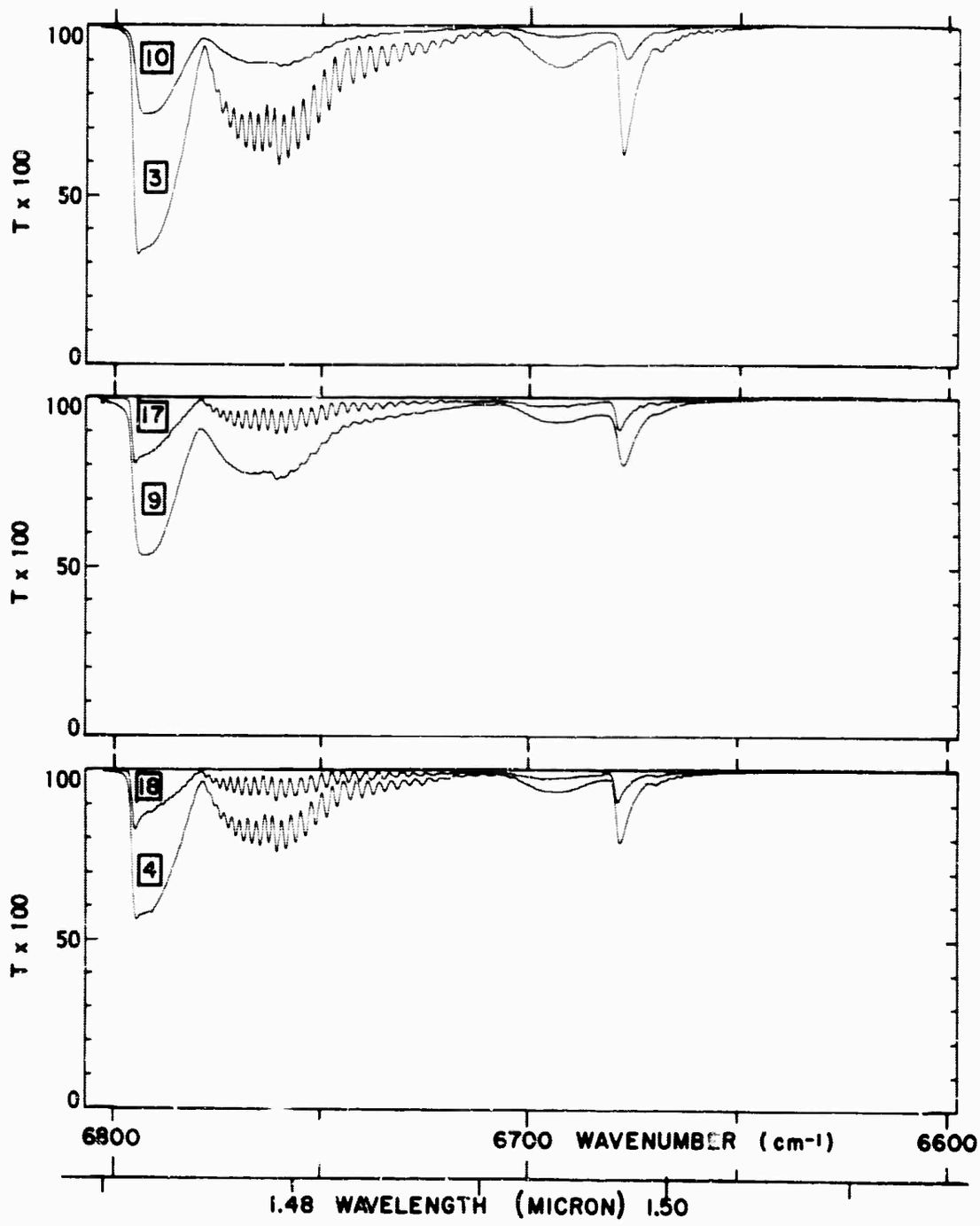
6700 WAVENUMBER (cm-1)
6600
1.48 WAVELENGTH (MICRON) 1.50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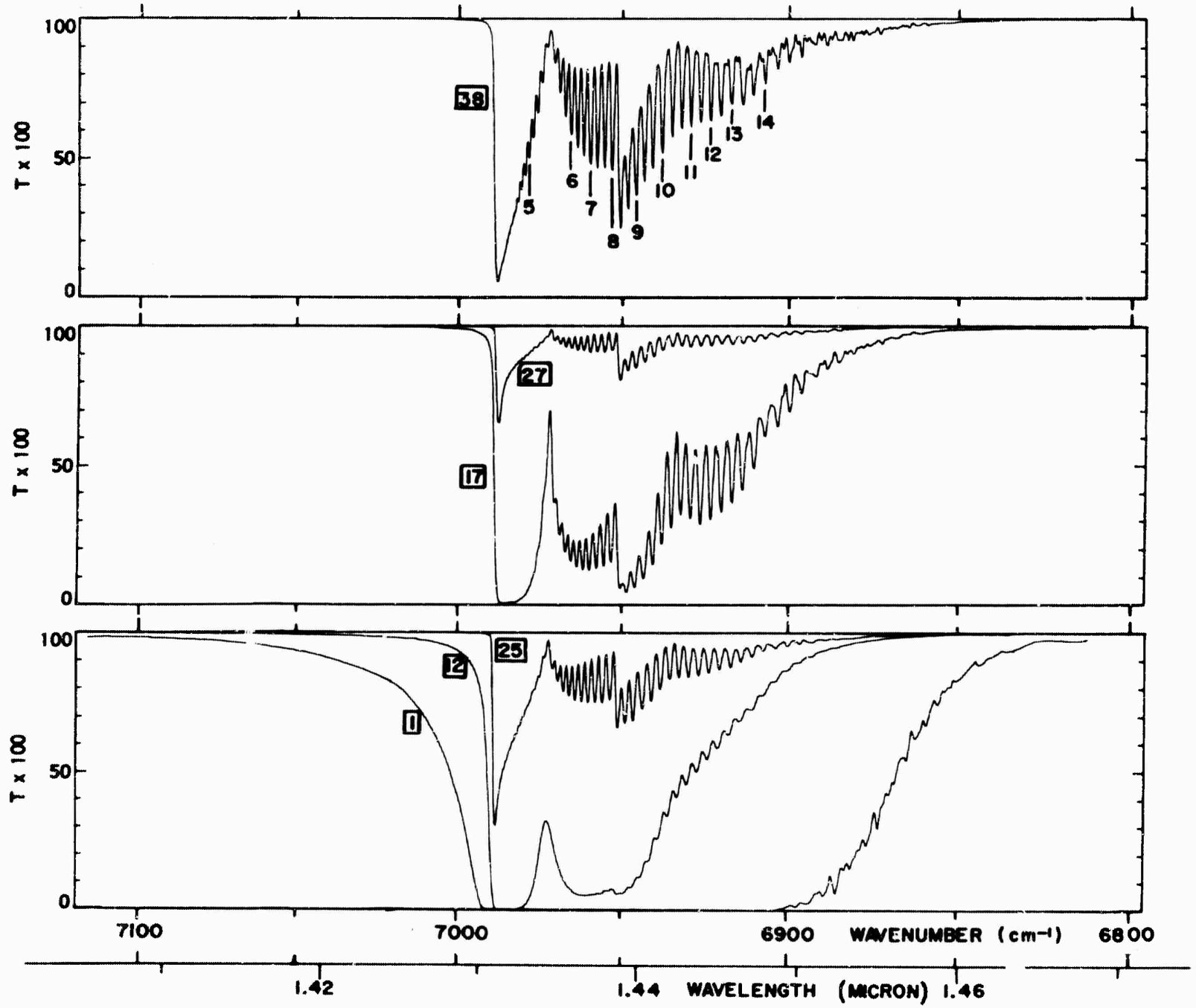
6700 WAVENUMBER (cm-1)
6600
1.48 WAVELENGTH (MICRON) 1.50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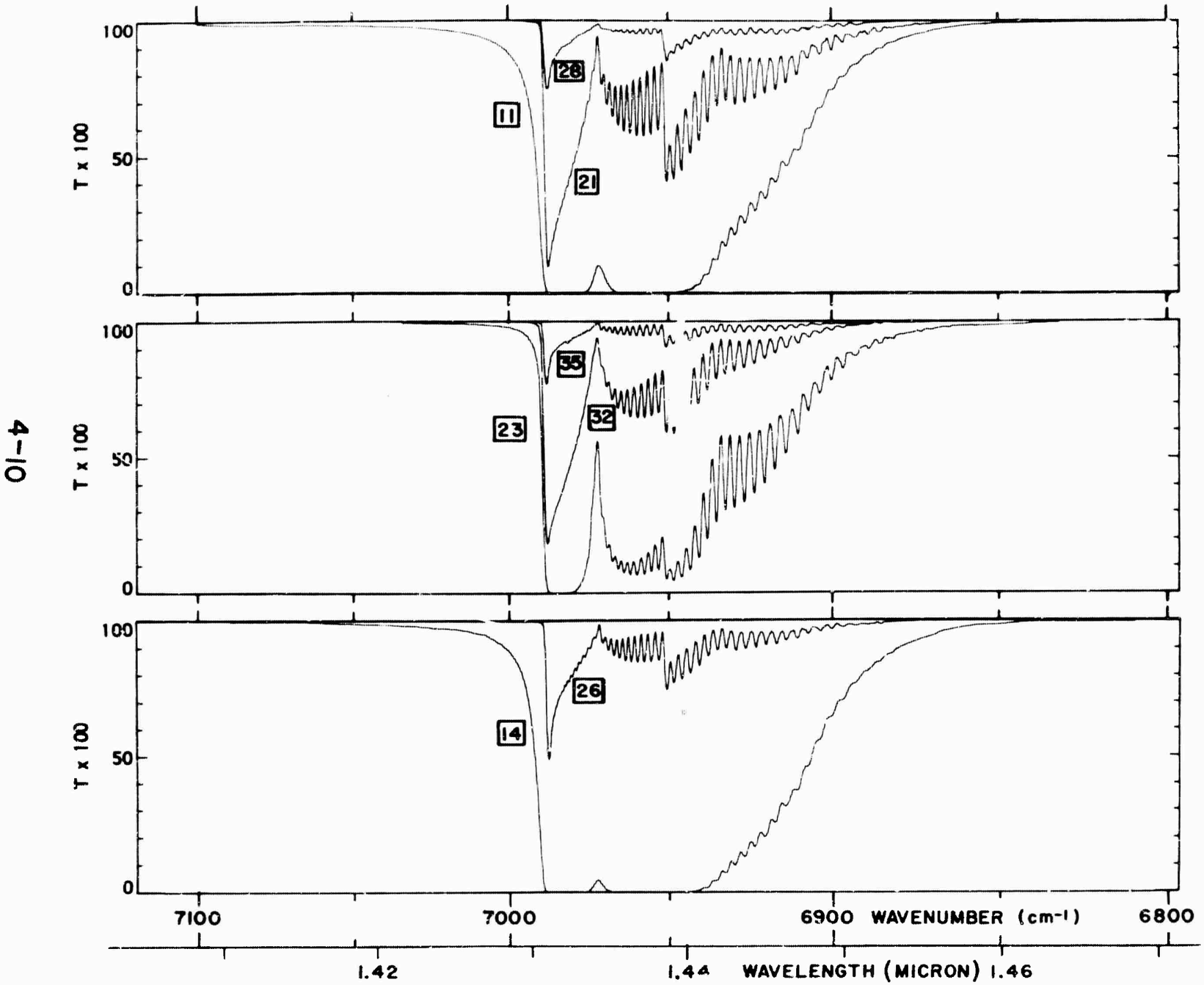
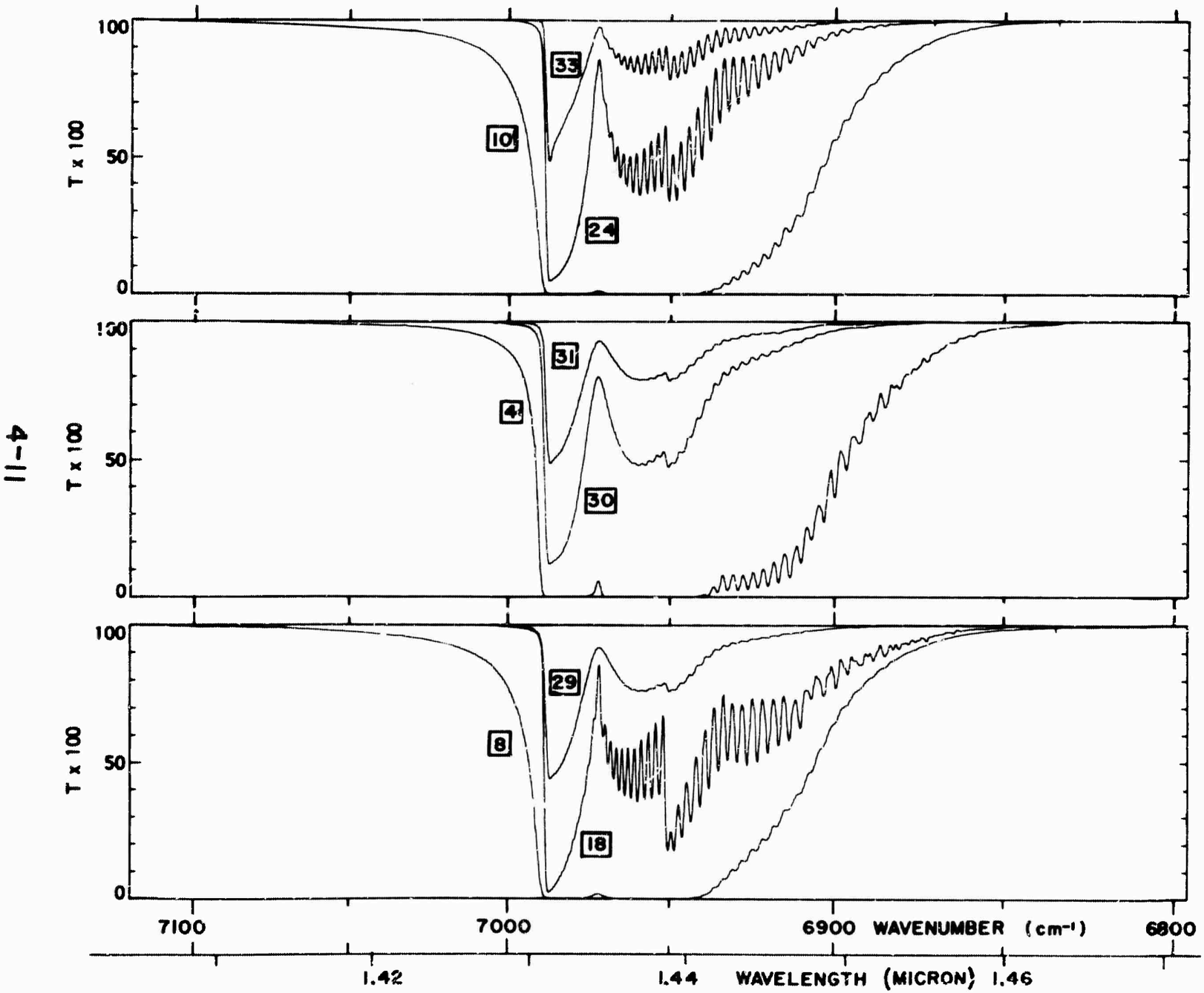
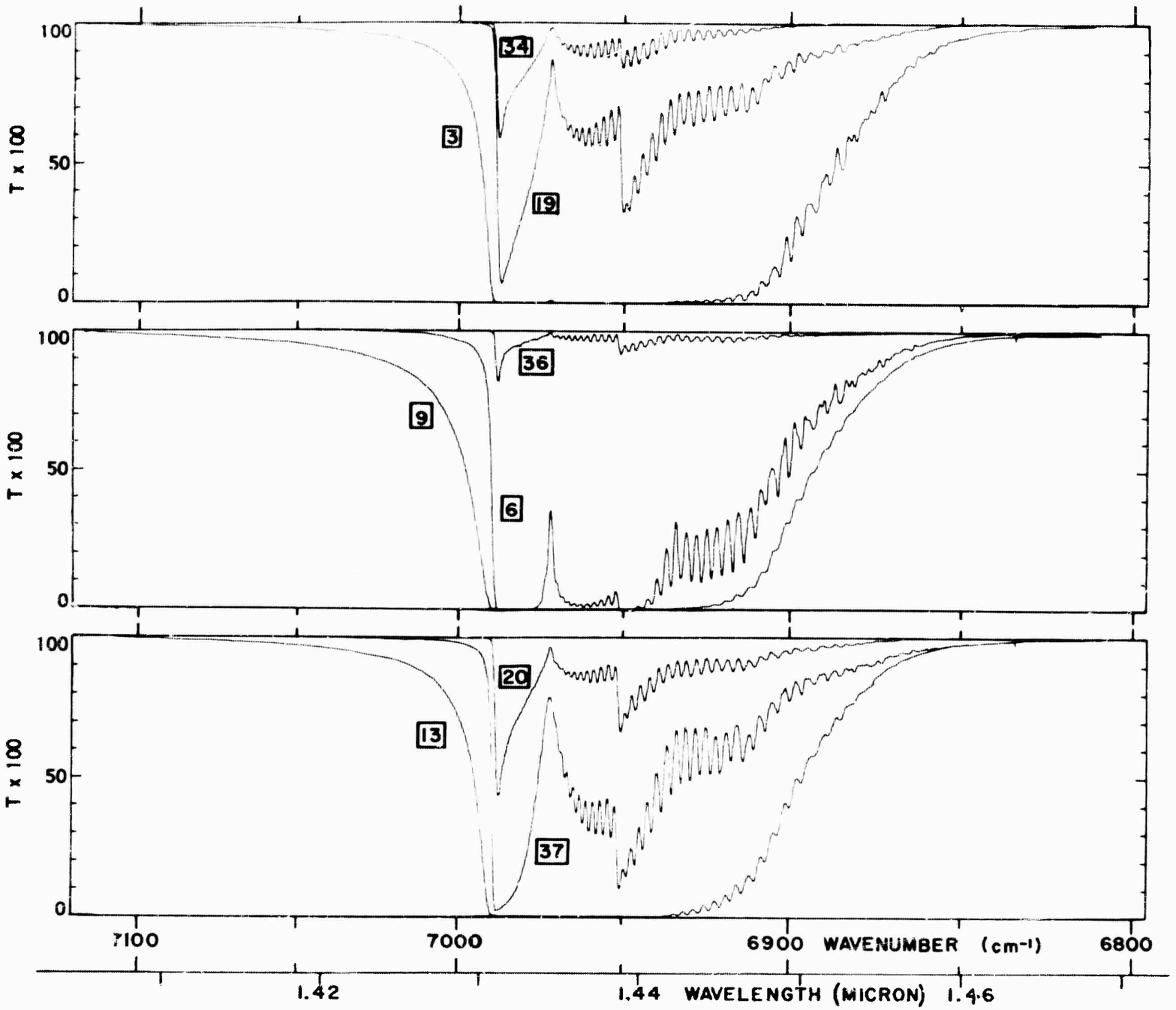
10
11
12
13
14
27
17
12
25
1
7100
7000
6900
6800
WAVENUMBER (cm⁻¹)
1.42
1.44
1.46
WAVELENGTH (MICRON)


100
50
0
T x 100
11
28
21
23
55
32
14
26
7100
7000
6900
6800
WAVENUMBER (cm⁻¹)
1.42
1.44
1.46
WAVELENGTH (MICRON)


100
50
0
T x 100
33
10
24
31
4
30
29
8
18
7100
7000
6900 WAVENUMBER (cm⁻¹)
6800
1.42
1.44
WAVELENGTH (MICRON)
1.46


100
50
0
T x 100
34
3
19
36
9
6
20
13
37
7100
7000
6900
6800
WAVENUMBER (cm⁻¹)
1.42
1.44
1.46
WAVELENGTH (MICRON)

SECTION 5

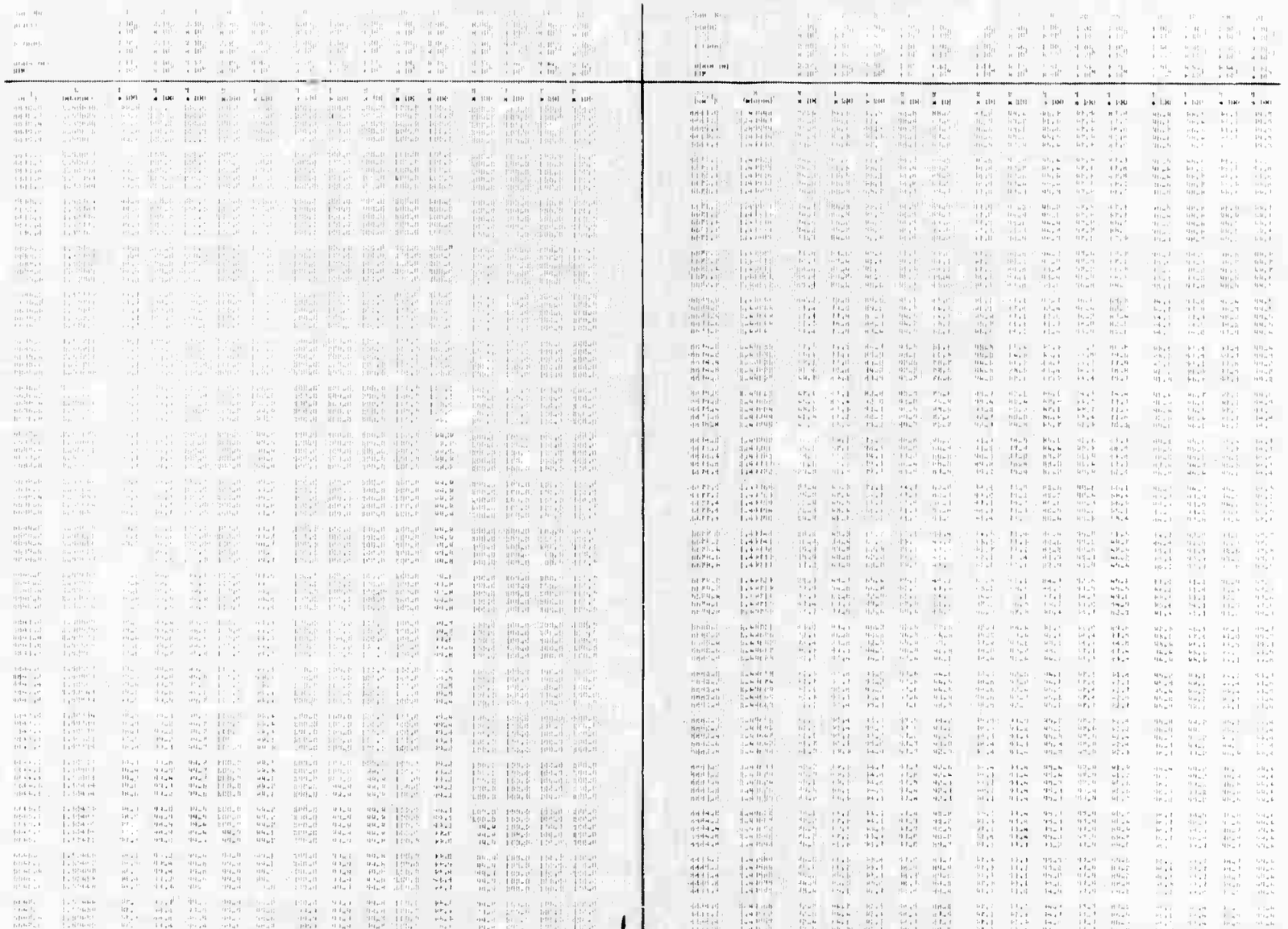
TABLE OF TRANSMITTANCES

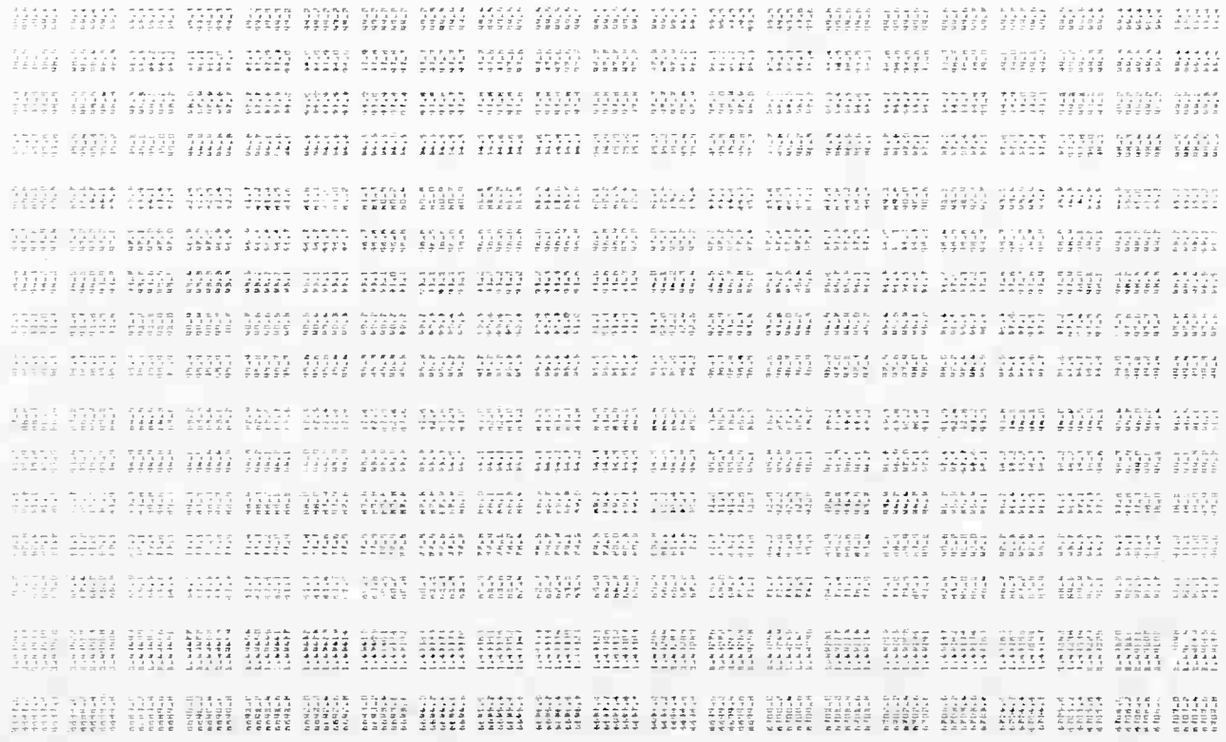
Tables 5-1 and 5-2 consist of values of transmittance, in percent, recorded at intervals of 0.2 cm^{-1} in the region from 6630 to 6806 cm^{-1} and from 6813 to 7125 cm^{-1}, respectively. The 0.2 cm^{-1} interval is sufficiently small that the original spectra could be approximated very closely by plotting the tabulated values and joining the points with straight lines. The first column gives the wavenumber in cm^{-1}, and the second column gives the corresponding wavelength in microns. The tables were made by stripping and photographing portions of the computer output which was obtained from the spectra by the technique described in Section 2.

The CO_2 partial pressure p, the total pressure P due to $CO_2 + N_2$, and the absorber thickness u for each sample are shown at the top of the column corresponding to that sample. These parameters are repeated on alternate pages for convenience. Each sample is designated by the same number as in Table 4-1 and in the spectra in Section 4. All samples were at 296°K, with the exception of 37 and 38 which were at 431°K.

Values of transmittance are not tabulated over regions of small absorptance ($T \cong 1$) for some of the samples. The absorptance between 6806 and 6813 cm^{-1} is completely negligible except for a few of the largest samples. For these samples it is safe to assume that the absorptance varies linearly between the values tabulated at 6806 and 6813 cm^{-1}. All values for a given wavenumber appear on a single page.

Table 5-1





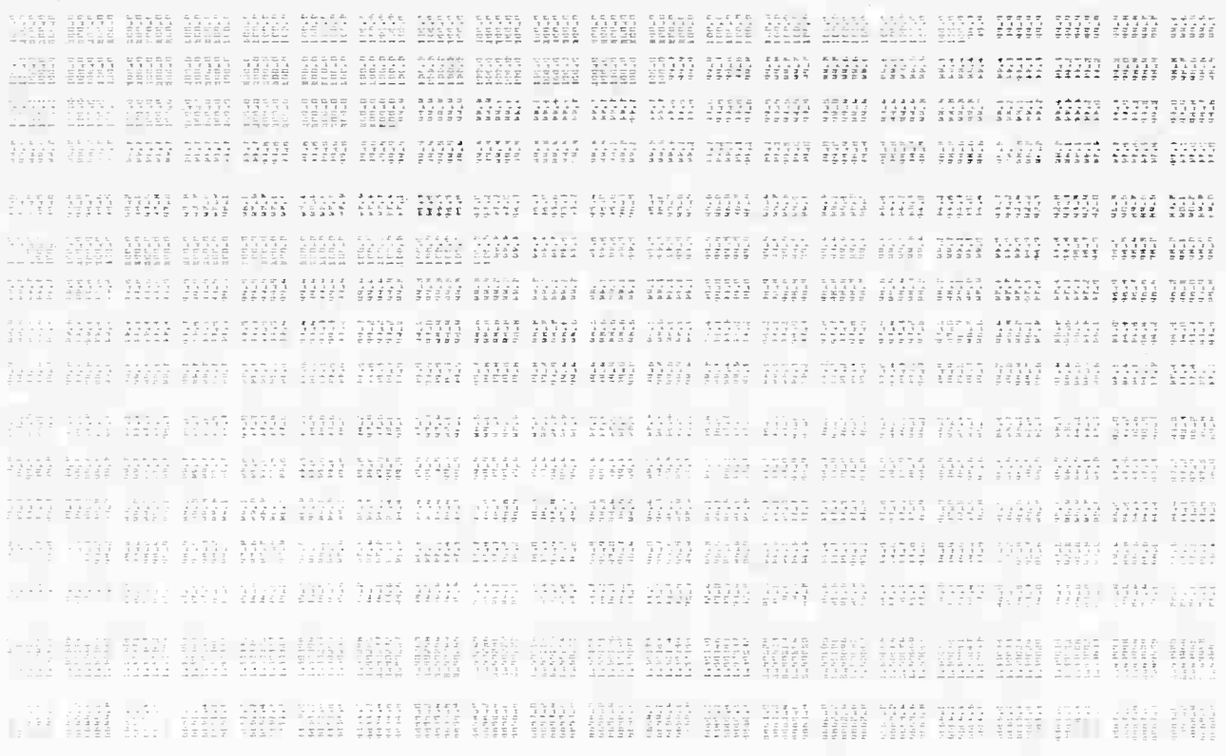
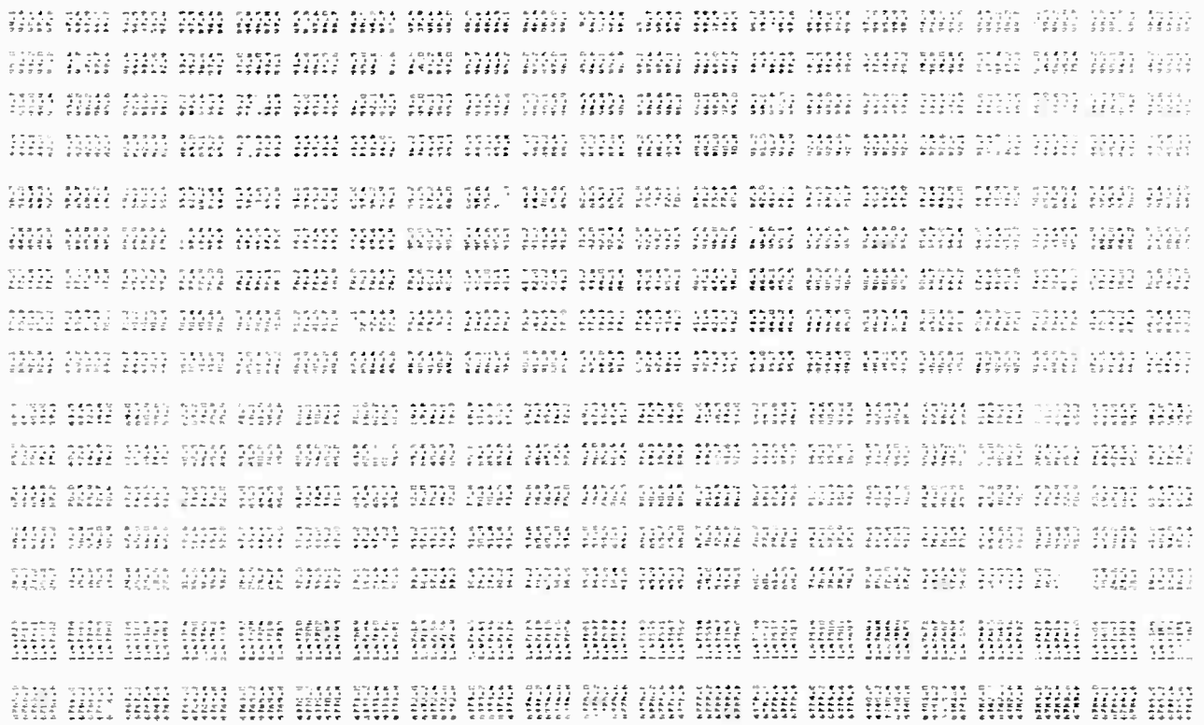


Table 5-1 (continued)



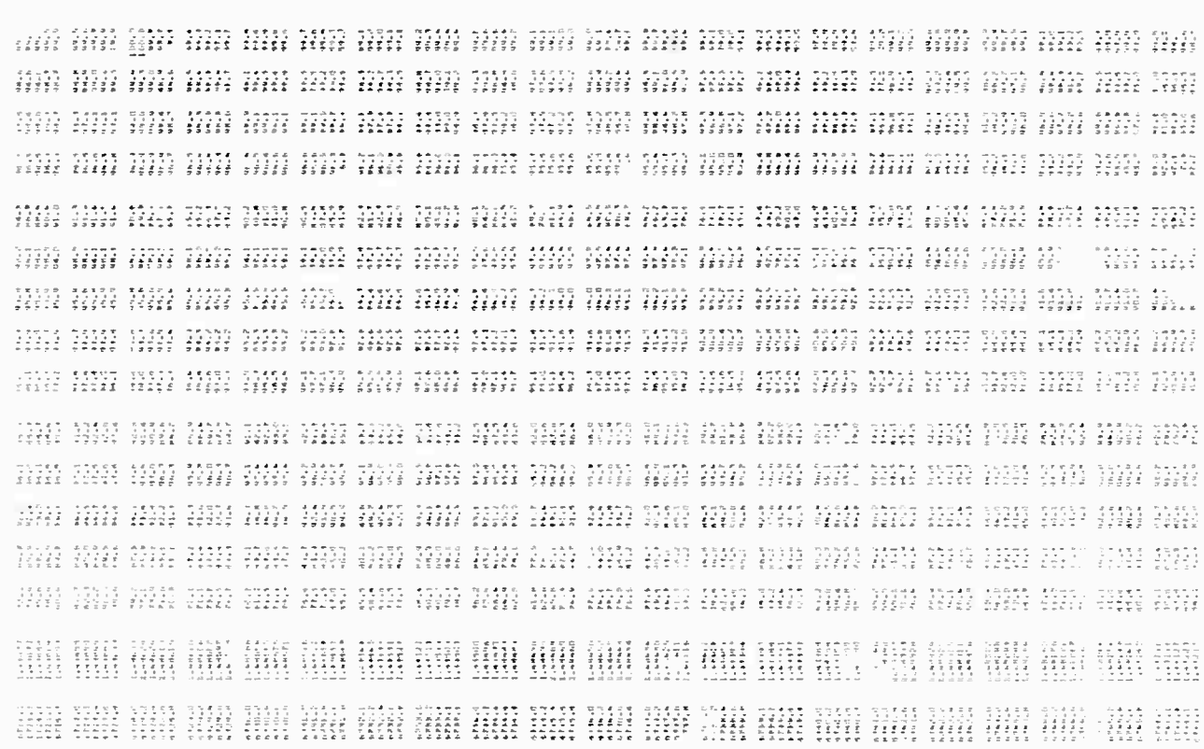


Table 5-1 (continued)

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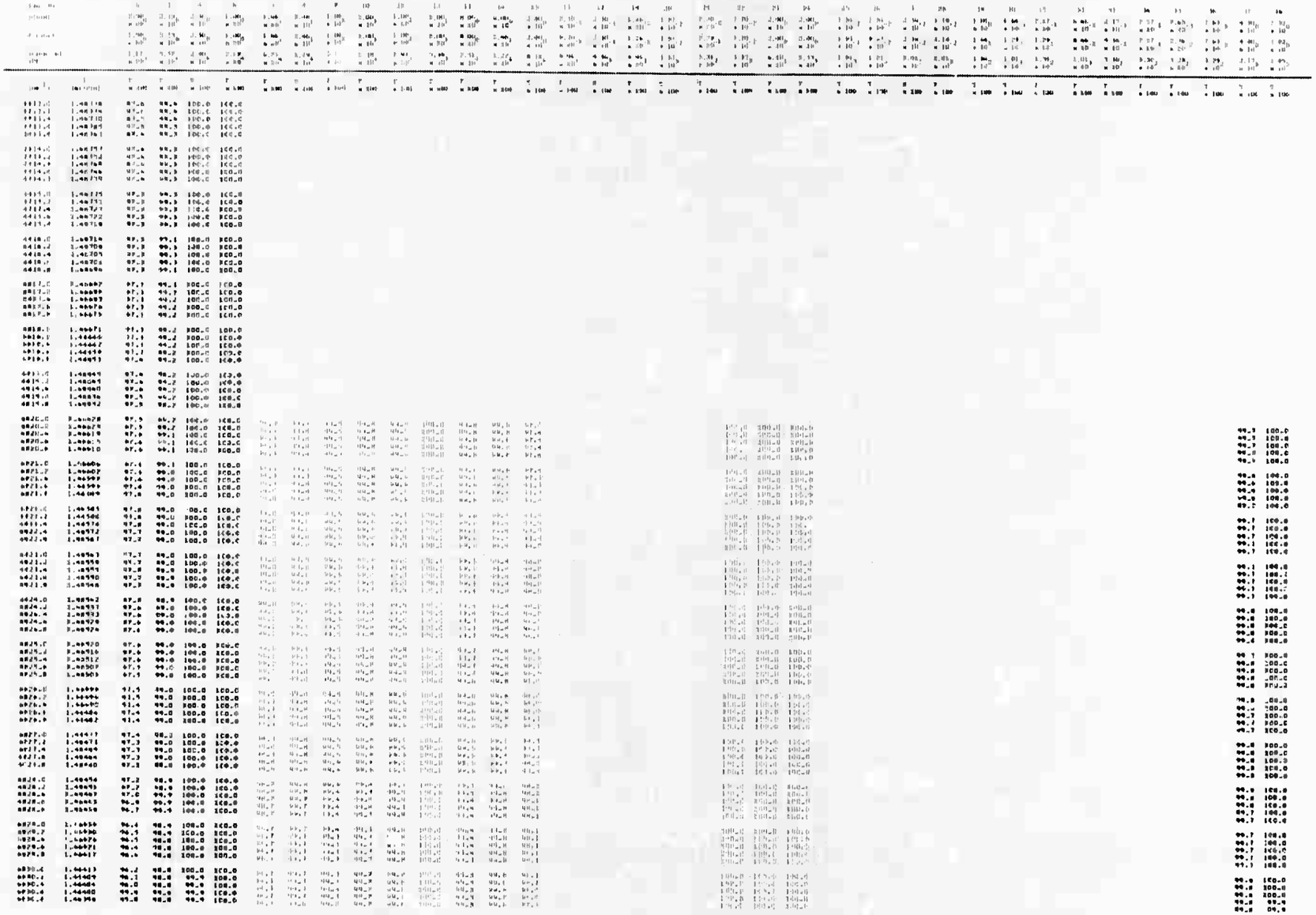
Table 5-2



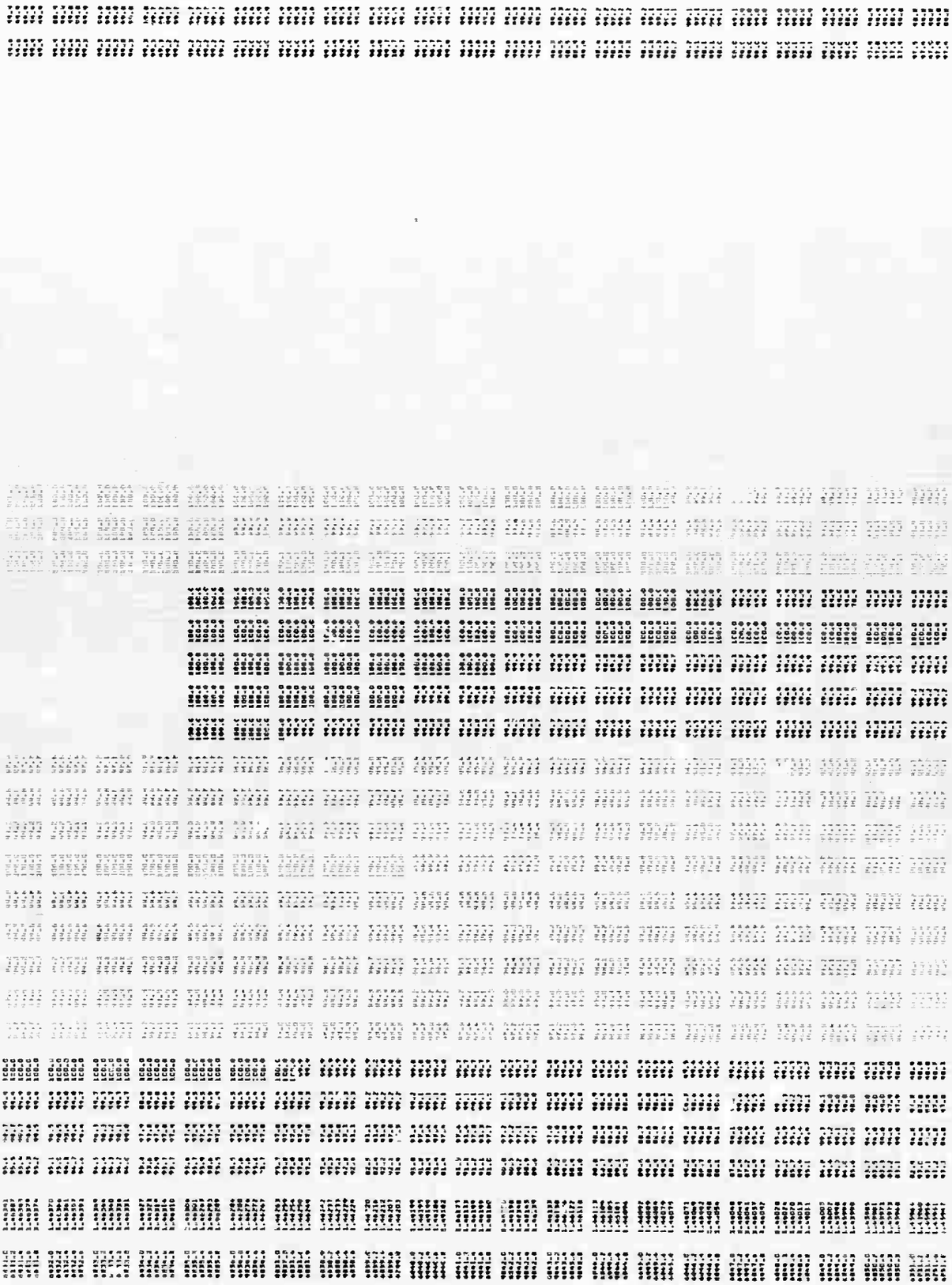


Table 5-2 (continued)

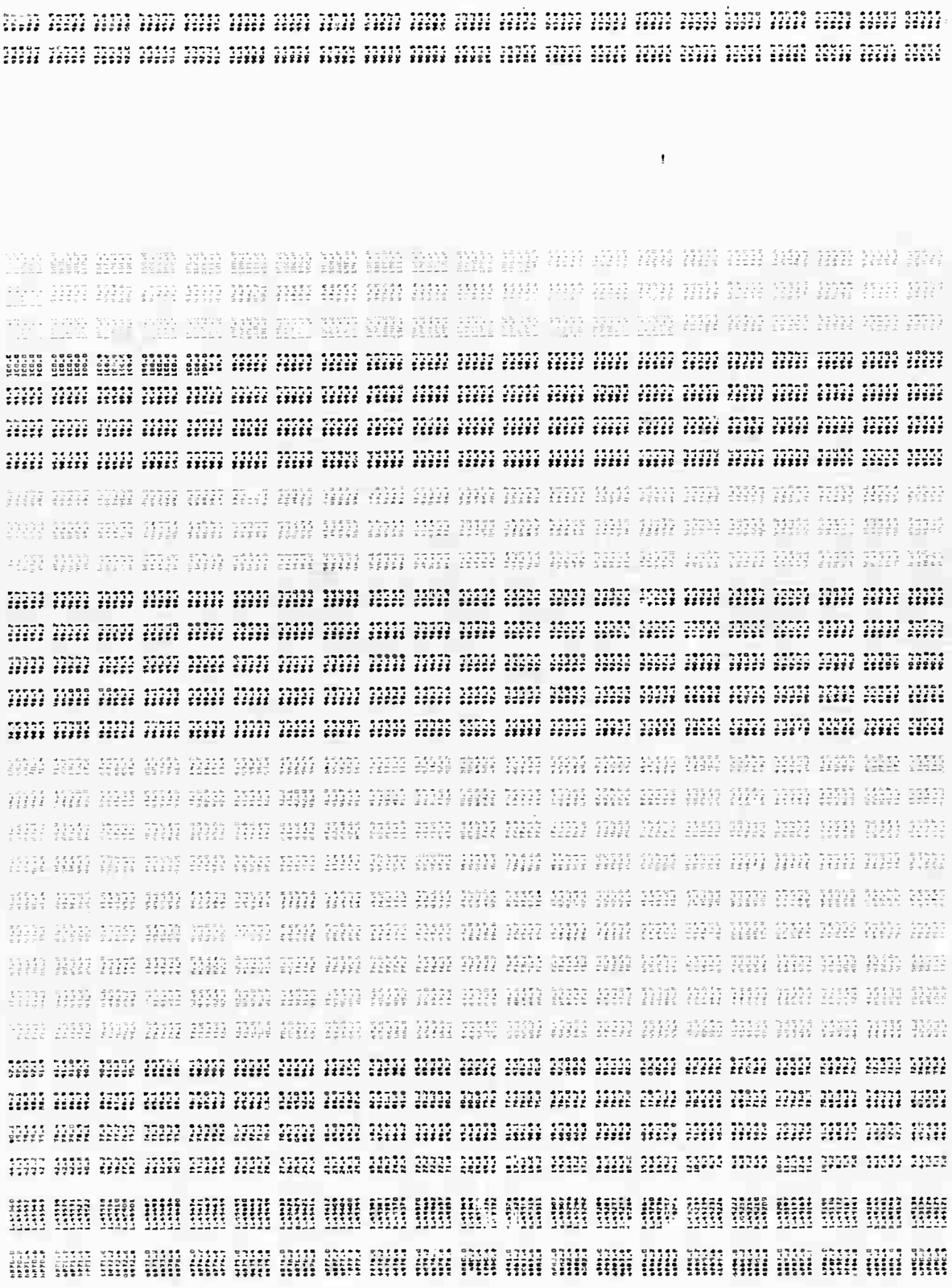
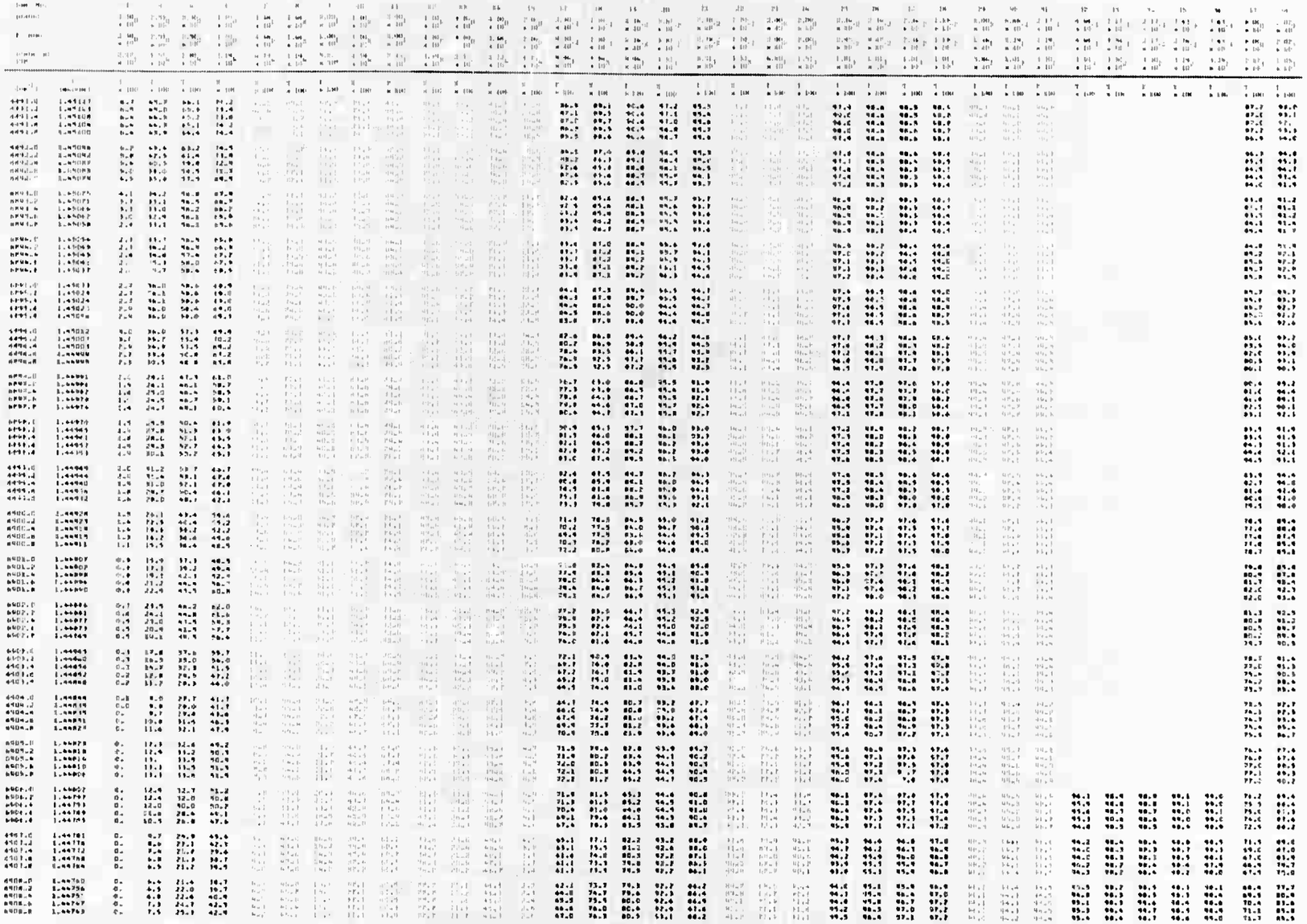


Table 5-2 (continued)



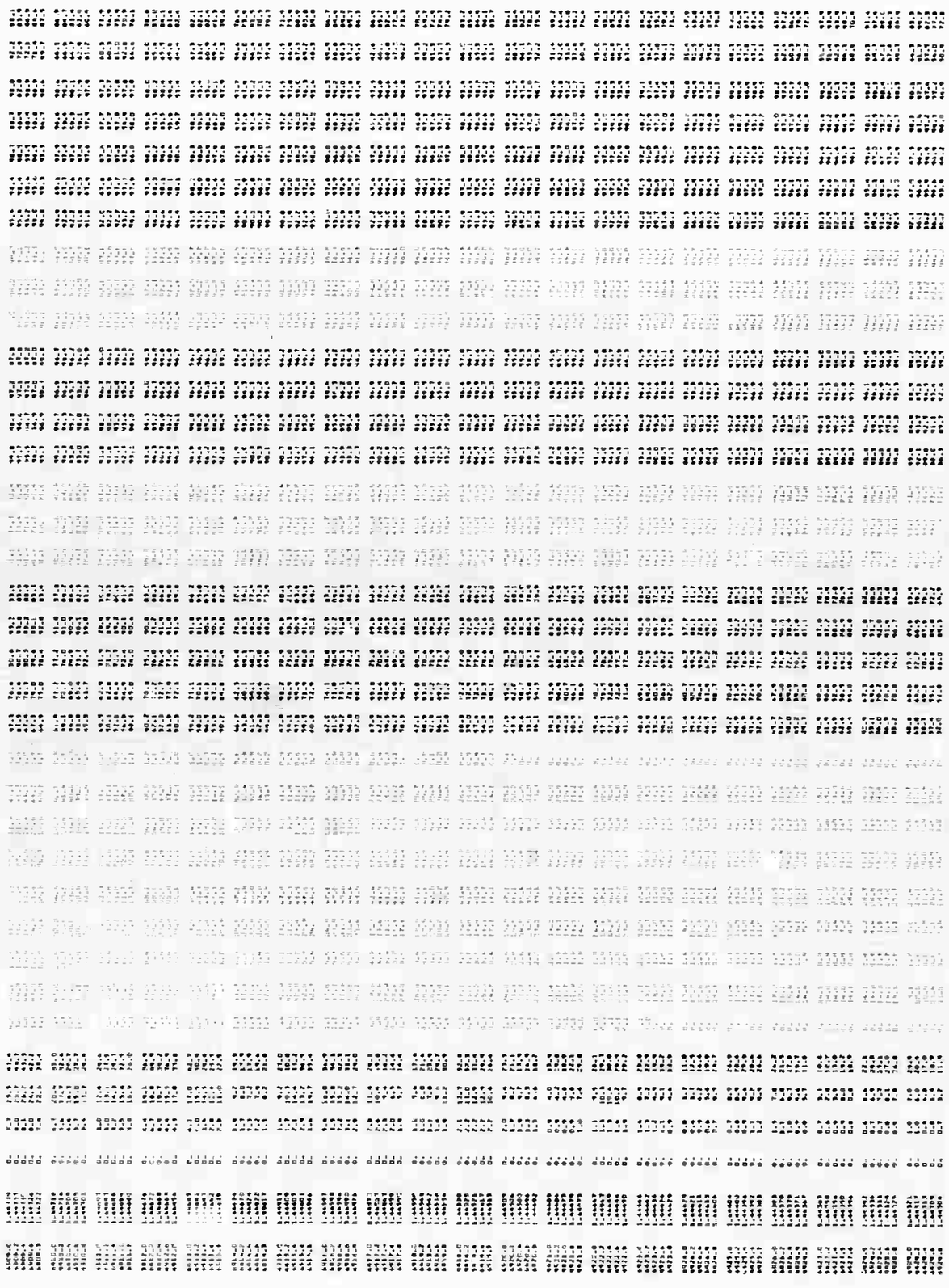
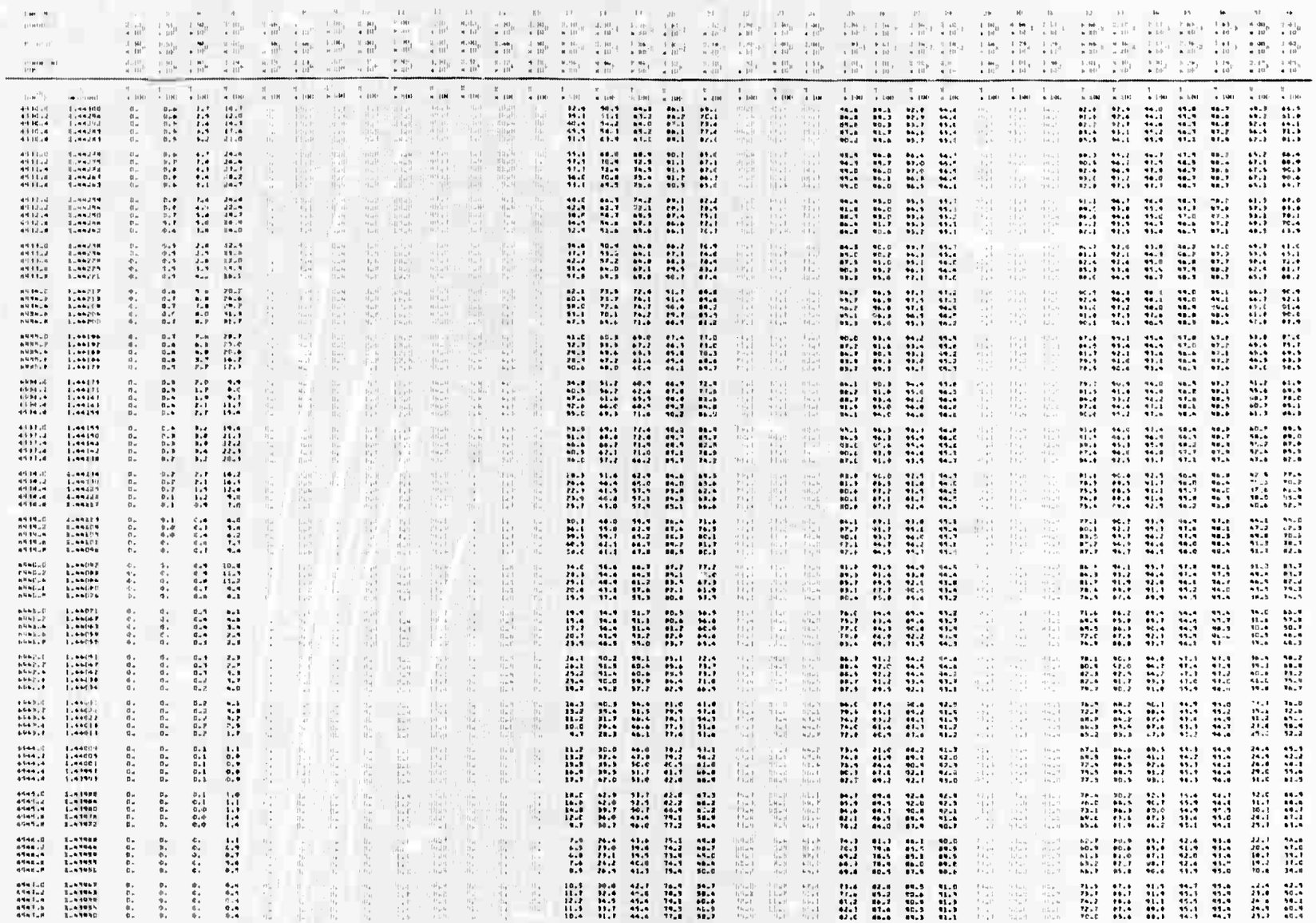


Table 5-2 (continued)



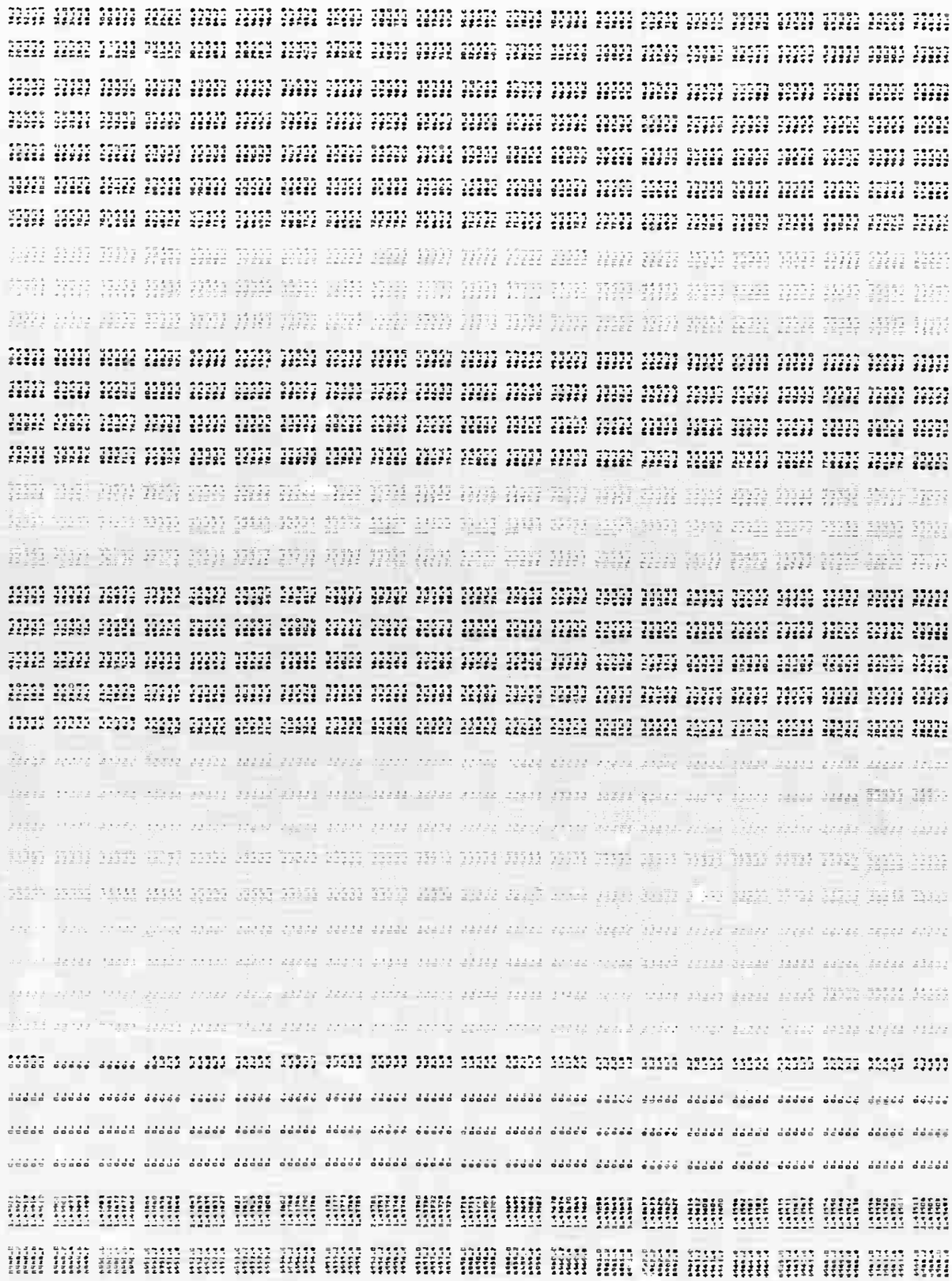
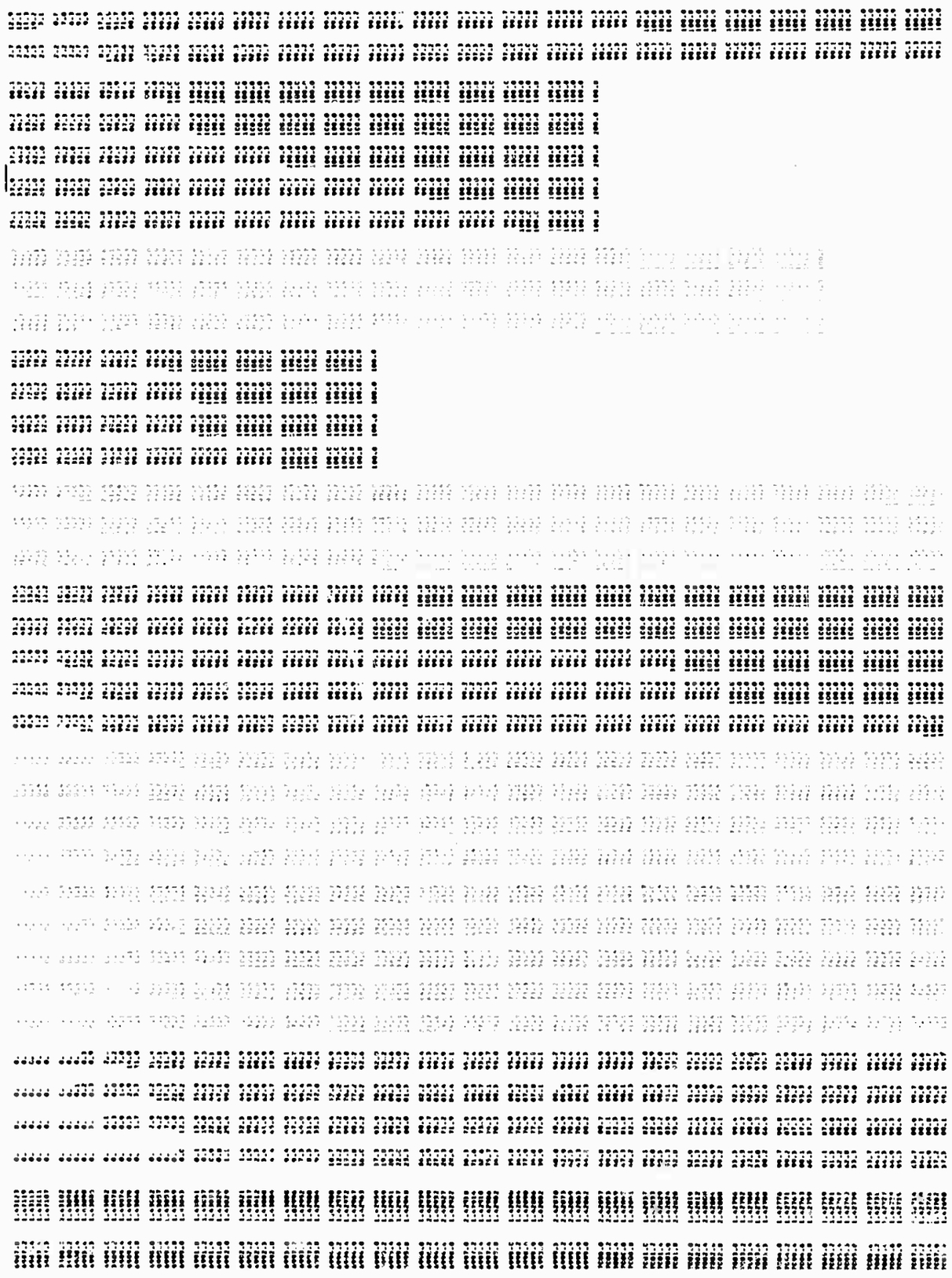


Table 5-2 (continued)



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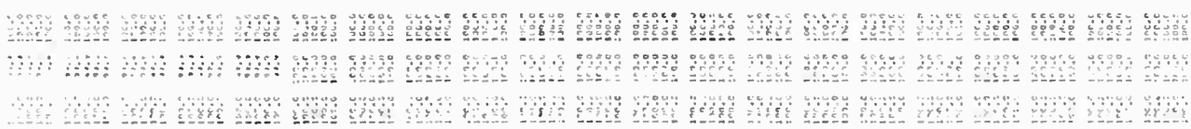


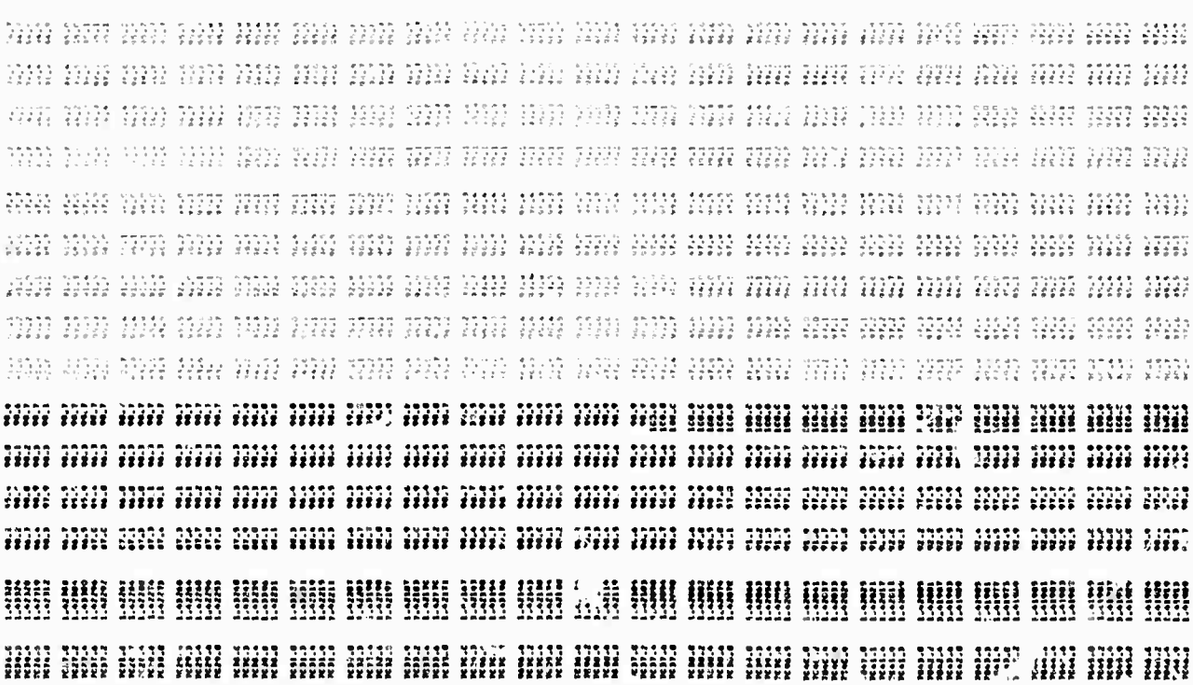
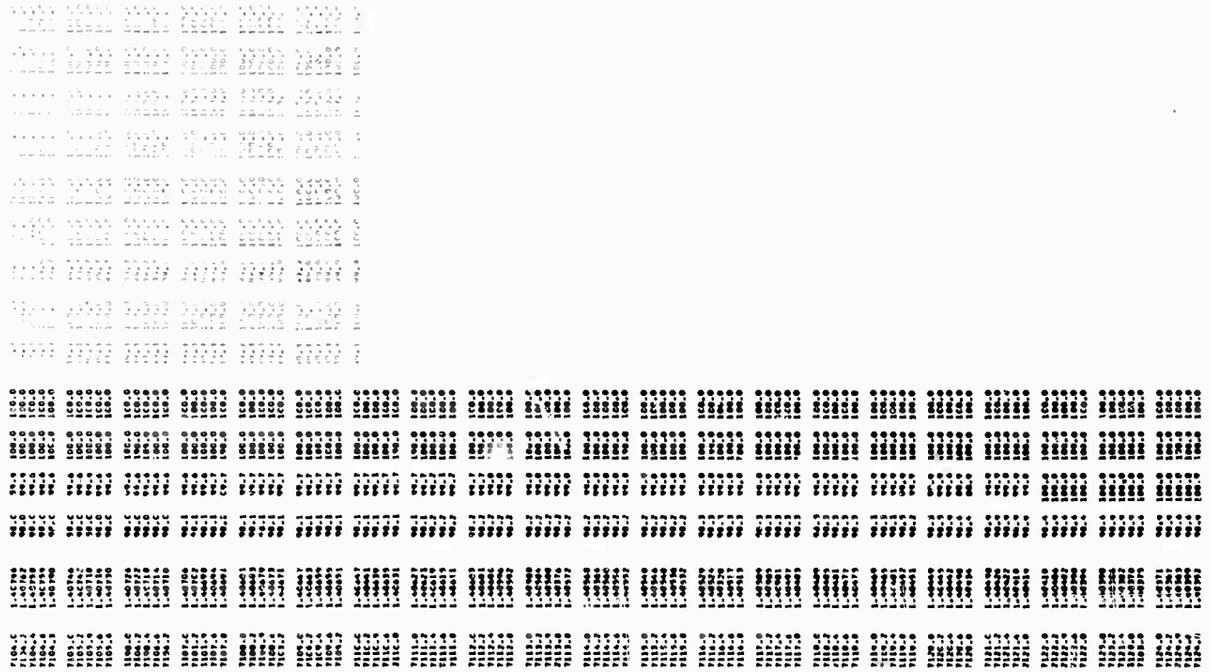
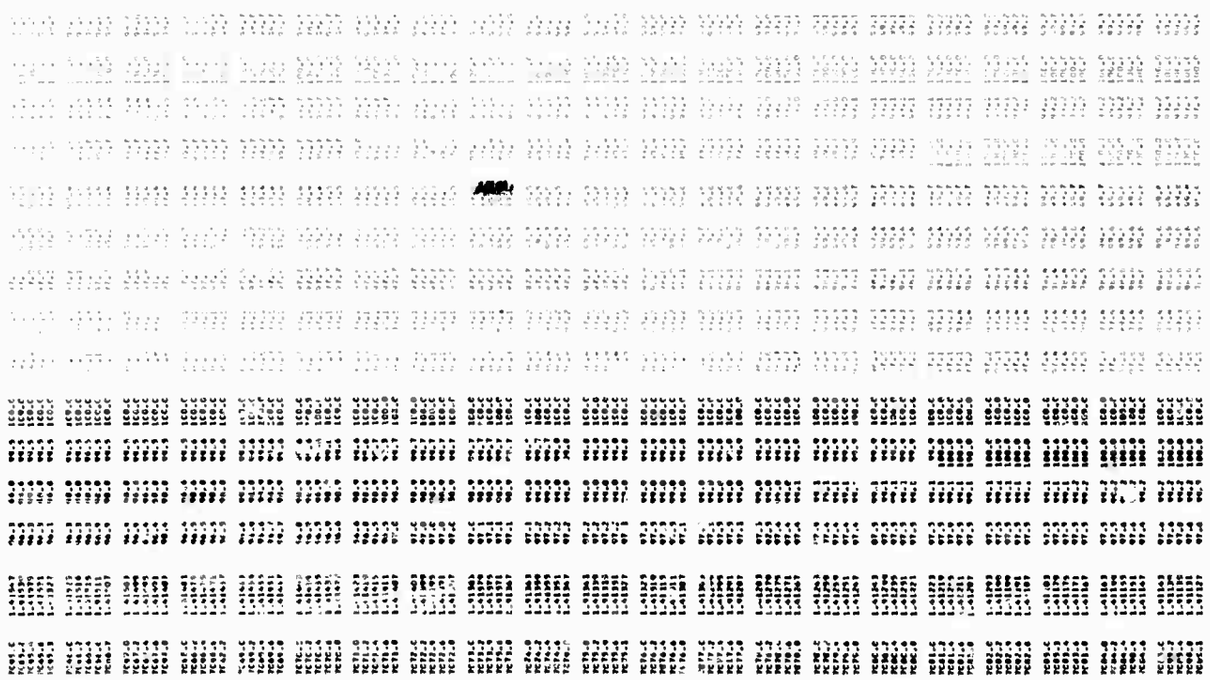


Table 5-2 (continued)





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SECTION 6

TABLES OF INTEGRATED ABSORPTANCE

Values of the integrated absorptance are presented in Tables 6-1 and 6-2 for the regions below and above 6806 cm^{-1}, respectively. The tables do not cover the entire interval for all the samples. In general, the tables include only the region over which the absorptance is great enough to be measured with reasonable accuracy. The calculations were usually made for groups of from 3 to 5 samples at a time with the limits of integration the same for all the samples in a given group. The lower limit of integration ν', which is shown at the top of each column, was chosen at a point below which there was little absorption.

The integrated absorptance between any two wavenumbers listed can be found by subtracting the values tabulated at the two points. All of the significant figures are carried in the table in order to avoid losing information when dealing with narrow intervals. The table was formed by stripping and photographing part of the computer output with the proper headings pieced in above each section.

Over a portion of Table 6-2 there are too many values listed at a given wavenumber to include them all on one page. Therefore, they were arranged to appear on successive pages which can be seen simultaneously.

In regions where the structure in the spectra is regular, the integrated absorptance was calculated at wavenumbers midway between the line centers. Therefore, in the case of no overlapping, the difference between

two successive tabulated values is the equivalent width of the absorption line in the interval. In some other regions where the structure was not particularly regular, the integrated absorptance was calculated at wavenumbers corresponding to absorptance minima. In still other regions where there was but little structure or where the absorptance minima would shift as the pressure or absorber thickness was changed, the values were calculated at integral wavenumbers or possibly at integral half-wavenumbers, depending on the amount of information one might expect to obtain from closer readings.

The important parameters for each sample are shown at the top of the column corresponding to that sample. All samples were at 296°K, with the exception of 37 and 38 which were at 431°K.

Table 6-1 $\left[\int_{\nu'}^{\nu} A(\nu)\, d\nu\right]$

Sam. No.	1	2	3	4	5	6	7	8	10	15	16	17	18	22
p(atm)	$2.50_0 \times 10^0$	$2.53_0 \times 10^0$	$2.53_0 \times 10^0$	$2.50_0 \times 10^0$	$1.00_0 \times 10^0$	$1.00_0 \times 10^0$	$1.46_1 \times 10^{-1}$	$1.00_1 \times 10^{-1}$	$1.00_1 \times 10^{-1}$	$2.00_0 \times 10^0$	$8.00_0 \times 10^0$	2.30×10^{-1}	2.30×10^{-1}	7.70×10^{-2}
P (atm)	$2.50_0 \times 10^0$	$2.53_0 \times 10^0$	$2.53_0 \times 10^0$	$2.50_0 \times 10^0$	$1.00_0 \times 10^0$	$1.00_0 \times 10^0$	$1.46_1 \times 10^{-1}$	$1.00_1 \times 10^{-1}$	$1.00_1 \times 10^{-1}$	$2.00_0 \times 10^0$	$1.46_1 \times 10^{-1}$	3.30×10^{-1}	2.30×10^{-1}	7.70×10^{-2}
u(atm cm) STP	$2.17_5 \times 10^3$	$1.19_9 \times 10^3$	$5.57_4 \times 10^4$	$2.80_4 \times 10^4$	$9.63_2 \times 10^5$	$2.13_6 \times 10^6$	$6.73_4 \times 10^4$	$3.15_7 \times 10^4$	$1.54_6 \times 10^4$	8.71×10^4	2.51×10^4	3.96×10^3	9.96×10^3	3.32×10^3
(cm^{-1})	$\nu'=6640$ cm^{-1}	$\nu'=6640$ cm^{-1}	$\nu'=6640$ cm^{-1}	$\nu'=6640$ cm^{-1}	$\nu'=6640$ cm^{-1}	$\nu'=6640$ cm^{-1}	$\nu'=6640$ cm^{-1}	$\nu'=6640$ cm^{-1}	$\nu'=6640$ cm^{-1}	$\nu'=6640$ cm^{-1}	$\nu'=6640$ cm^{-1}	$\nu'=6640$ cm^{-1}	$\nu'=6640$ cm^{-1}	$\nu'=6640$ cm^{-1}
6640.0	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
6645.0	0.048	0.027	0.012	0.000	0.029	0.	0.001	0.001	0.	0.026	0.	0.	0.	0.
6651.0	0.222	0.122	0.057	0.013	0.134	0.009	0.013	0.022	0.	0.126	0.015	0.	0.	0
6656.1	0.325	0.171	0.081	0.022	0.159	0.017	0.027	0.034	0.	0.179	0.023	0.000	0.	0.
6659.3	0.445	0.231	0.113	0.033	0.208	0.027	0.049	0.051	0.006	0.243	0.035	0.002	0.	0.
6658.5	0.389	0.338	0.151	0.046	0.265	0.035	0.076	0.067	0.006	0.330	0.051	0.007	0.	0.
6660.6	0.741	0.389	0.188	0.061	0.331	0.046	0.104	0.096	0.016	0.413	0.067	0.014	0.002	0.
6662.7	0.933	0.488	0.250	0.081	0.407	0.059	0.153	0.112	0.027	0.505	0.088	0.025	0.008	0.
6664.7	1.169	0.605	0.286	0.107	0.508	0.075	0.210	0.146	0.042	0.611	0.114	0.038	0.018	0.000
6666.7	1.474	0.764	0.366	0.143	0.632	0.100	0.290	0.195	0.064	0.750	0.148	0.054	0.032	0.002
6668.6	1.81	0.982	0.471	0.192	0.798	0.136	0.396	0.262	0.097	0.935	0.197	0.073	0.053	0.008
6670.4	2.31	1.243	0.601	0.256	1.006	0.192	0.521	0.341	0.135	1.159	0.257	0.100	0.078	0.016
6672.3	2.86	1.521	0.737	0.324	1.206	0.259	0.667	0.439	0.173	1.391	0.330	0.129	0.100	0.021
6674.8	3.300	4.441	2.436	1.221	3.598	0.962	2.060	1.444	0.671	3.899	1.093	0.488	0.437	0.131
6681.3	7.664	4.623	2.556	1.286	3.776	1.014	2.201	1.545	0.716	4.151	1.184	0.518	0.465	0.142
6683.7	8.112	4.864	2.674	1.344	3.962	1.051	2.369	1.659	0.771	4.343	1.276	0.537	0.488	0.136
6686.2	8.220	4.923	2.702	1.357	3.982	1.061	2.402	1.642	0.782	4.394	1.292	0.542	0.494	0.159
6685.5	8.532	5.095	2.785	1.395	4.112	1.093	2.488	1.745	0.809	4.528	1.337	0.558	0.511	0.167
6686.8	8.805	5.296	2.983	1.442	4.265	1.130	2.581	1.814	0.834	4.692	1.388	0.578	0.530	0.175
6688.1	9.280	5.526	2.998	1.497	4.437	1.174	2.683	1.888	0.870	4.878	1.444	0.598	0.550	0.183
6689.3	9.686	5.753	3.117	1.557	4.615	1.222	2.786	1.962	0.904	5.067	1.501	0.618	0.569	0.190
6690.5	10.116	6.006	3.245	1.621	4.810	1.272	2.899	2.041	0.940	5.271	1.562	0.641	0.592	0.199
6691.6	10.525	6.243	3.373	1.686	4.996	1.318	2.999	2.115	0.975	5.472	1.620	0.666	0.614	0.207
6693.0	11.044	6.555	3.542	1.768	5.236	1.380	3.132	2.211	1.021	5.734	1.696	0.696	0.643	0.218
6695.0	11.844	7.004	3.785	1.889	5.582	1.475	3.327	2.350	1.089	6.118	1.806	0.738	0.688	0.232
6697.0	12.594	7.432	4.014	2.007	5.919	1.568	3.510	2.483	1.157	6.490	1.912	0.782	0.736	0.242
6699.0	13.276	7.814	4.212	2.114	6.238	1.650	3.672	2.604	1.216	6.835	2.008	0.826	0.778	0.252
6701.0	13.862	8.129	4.371	2.200	6.494	1.718	3.799	2.703	1.266	7.122	2.092	0.865	0.812	0.262
6703.0	14.280	8.369	4.491	2.264	6.702	1.768	3.898	2.777	1.305	7.338	2.157	0.893	0.841	0.270
6707.0	14.759	8.649	4.626	2.333	6.919	1.822	4.012	2.873	1.353	7.605	2.248	0.935	0.878	0.291
6710.9	15.162	8.849	4.716	2.367	7.084	1.859	4.092	2.933	1.380	7.809	2.361	0.961	0.899	0.307
6714.4	15.393	9.024	4.796	2.402	7.213	1.899	4.158	2.995	1.410	7.979	2.351	0.991	0.926	0.319
6717.7	15.744	9.232	4.893	2.462	7.365	1.932	4.261	3.066	1.437	8.162	2.404	1.017	0.931	0.328
6721.1	16.243	9.524	5.042	2.506	7.579	1.978	4.400	3.162	1.476	8.402	2.475	1.047	0.957	0.338
6724.3	16.615	9.694	5.214	2.582	7.830	2.054	4.557	3.270	1.522	8.672	2.562	1.078	0.990	0.344
6727.5	17.517	10.294	5.421	2.679	8.148	2.141	4.748	3.399	1.580	8.996	2.667	1.114	1.025	0.356
6730.6	18.242	10.665	5.629	2.776	8.452	2.219	4.931	3.537	1.639	9.343	2.772	1.151	1.058	0.370
6733.6	19.042	11.124	5.865	2.890	8.791	2.312	5.168	3.690	1.704	9.741	2.886	1.195	1.093	0.391
6736.6	19.896	11.631	6.121	3.020	9.167	2.413	5.411	3.859	1.779	10.152	3.014	1.252	1.138	0.412
6739.3	20.792	12.167	6.399	3.160	9.556	2.519	5.671	4.044	1.863	10.610	3.155	1.315	1.186	0.428
6742.3	21.721	12.716	6.698	3.306	9.961	2.661	5.949	4.237	1.957	11.089	3.307	1.376	1.236	0.460
6745.0	22.653	13.297	7.008	3.464	10.361	2.799	6.266	4.447	2.061	11.588	3.476	1.436	1.280	0.452
6747.7	23.692	13.955	7.370	3.646	10.770	2.924	6.635	4.707	2.196	12.142	3.672	1.512	1.332	0.470
6750.3	24.935	14.769	7.837	3.890	11.325	3.110	7.092	5.028	2.368	12.757	3.918	1.607	1.405	0.494
6752.6	26.369	15.721	8.394	4.180	11.982	3.368	7.634	5.419	2.563	13.573	4.207	1.726	1.498	0.524
6755.3	27.983	16.819	9.063	4.547	12.770	3.635	8.260	5.881	2.775	14.487	4.569	1.860	1.603	0.566
6757.7	29.648	17.981	9.779	4.948	13.603	3.928	8.949	6.386	3.028	15.368	4.928	2.021	1.728	0.618
6760.0	31.315	19.167	10.522	5.369	14.456	4.235	9.650	6.910	3.293	16.320	5.324	2.180	1.853	0.665
6762.3	32.979	20.366	11.286	5.803	15.324	4.548	10.357	7.446	3.566	17.555	5.739	2.364	1.988	0.712
6764.5	34.449	21.408	11.935	6.174	16.005	4.808	11.001	7.975	3.811	18.440	6.107	2.487	2.092	0.748
6766.6	35.933	22.458	12.588	6.552	16.706	5.073	11.729	8.389	4.065	19.305	6.462	2.618	2.191	0.788
6768.6	37.298	23.454	13.213	6.917	17.375	5.331	12.239	8.834	4.268	20.142	6.804	2.761	2.290	0.829
6770.6	38.695	24.450	13.834	7.273	18.046	5.581	12.745	9.270	4.487	20.981	7.137	2.875	2.385	0.864
6772.5	40.005	25.361	14.394	7.589	18.669	5.824	13.218	9.661	4.682	21.749	7.442	2.992	2.471	0.901
6774.3	41.208	26.171	14.860	7.862	19.236	6.030	13.768	10.002	4.850	22.432	7.702	3.086	2.545	0.927
6776.1	42.316	26.884	15.307	8.095	19.753	6.209	14.186	10.294	4.994	23.036	7.933	3.16	2.616	0.949
6777.7	43.140	27.387	15.602	8.254	20.130	6.326	14.466	10.515	5.099	23.464	8.105	3.222	2.664	0.963
6780.1	43.863	27.815	15.836	8.384	20.432	6.398	14.632	10.784	5.213	23.824	8.247	3.256	2.698	0.971
6782.0	44.541	28.225	16.042	8.482	20.668	6.458	15.162	10.958	5.302	24.097	8.436	3.281	2.716	0.975
6784.0	45.781	29.049	16.505	8.722	21.226	6.639	15.839	11.276	5.460	24.716	8.651	3.359	2.781	0.993
6786.0	47.378	30.214	17.224	9.126	22.045	8.953	16.314	11.744	5.709	25.668	8.988	3.493	2.895	1.026
6788.0	49.165	31.618	18.162	9.673	23.068	7.367	17.189	12.389	6.053	26.810	9.466	3.683	3.048	1.073
6790.0	51.053	33.193	19.286	10.349	24.249	7.874	18.225	13.174	6.484	28.173	10.067	3.932	3.238	1.133
6792.0	52.987	34.873	20.525	11.127	25.569	8.464	19.361	14.059	6.965	29.678	10.778	4.229	3.461	1.210
6794.0	54.943	36.607	21.825	11.960	26.988	9.104	20.524	14.982	7.510	31.266	11.536	4.557	3.709	1.294
6796.0	56.894	38.368	23.155	12.812	28.509	9.787	21.696	15.879	8.029	32.876	12.289	4.913	4.002	1.396
6798.0	58.800	40.278	23.937	13.379	29.547	10.212	22.680	16.295	8.285	33.796	12.730	5.097	4.179	1.460
6800.0	58.097	39.352	23.798	13.416	29.605	10.234	22.157	16.369	8.328	33.876	12.813	5.095	4.181	1.462
6802.0	58.165	39.390	24.020	13.425	29.617	10.240	22.194	16.401	8.344	33.917	12.844	5.095	4.181	1.462
6804.0	58.183	39.419	24.034	13.430	29.625	10.241	22.221	16.433	8.356	33.946	12.863	5.095	4.181	1.462
6806.0	58.221	39.443	24.046	13.436	29.628	10.241	22.241	16.453	8.364	33.976	12.876	5.095	4.181	1.462

Table 6-2 $\left[\int_{\nu'}^{\nu} A(\nu)\, d\nu\right]$

Sam. No.	1	3	4	6	7	8	9	10	11	12	13	14	15	17	18	19	20	21
p(xtm)	2.50 x 10^{0}	2.53 x 10^{0}	2.50 x 10^{0}	1.00 x 10^{0}	1.46 x 10^{1}	1.46 x 10^{1}	1.00 x 10^{1}	1.00 x 10^{1}	1.00 x 10^{1}	1.00 x 10^{1}	8.00 x 10^{0}	4.00 x 10^{0}	2.00 x 10^{0}	2.30 x 10^{-1}	2.30 x 10^{-1}	1.16 x 10^{-1}	5.87 x 10^{-2}	2.70 x 10^{-2}
P (atm)	2.50 10^{0}	2.53 x 10^{0}	2.50 x 10^{0}	1.00 x 10^{0}	1.46 x 10^{1}	1.46 x 10^{1}	1.00 x 10^{1}	1.00 x 10^{1}	1.00 x 10^{1}	1.00 x 10^{1}	8.00 x 10^{0}	1.46 x 10^{1}	2.00 x 10^{0}	9.30 x 10^{-1}	2.30 x 10^{-1}	1.16 x 10^{-1}	5.87 x 10^{-2}	2.79 x 10^{-1}
w(xtm cm) STP	2.17 x 10^{5}	5.57 x 10^{4}	2.80 x 10^{4}	7.79 x 10^{4}	4.73 x 10^{4}	1.19 x 10^{4}	3.17 x 10^{4}	1.59 x 10^{4}	7.93 x 10^{3}	3.99 x 10^{3}	2.51 x 10^{4}	1.22 x 10^{4}	6.71 x 10^{4}	9.96 x 10^{3}	9.96 x 10^{3}	9.96 x 10^{3}	3.32 x 10^{4}	3.32 x 10^{3}
(cm^{-1})	ν' 6820 cm^{-1}	ν' 6820 cm^{-1}	ν' 6820 cm^{-1}	ν' 6820 cm^{-1}	ν' 6820 cm^{-1}	ν' 6820 cm^{-1}	ν' 6820 cm^{-1}	ν' 6820 cm^{-1}	ν' 6820 cm^{-1}	ν' 6820 cm^{-1}	ν' 6820 cm^{-1}	ν' 6870 cm^{-1}	ν' 6820 cm^{-1}	ν' 6836 cm^{-1}	ν' 6836 cm^{-1}	ν' 6836 cm^{-1}	ν' 6836 cm^{-1}	ν' 6836 cm^{-1}
6830.0	0.262	0.102	0.000	0.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]					
6840.0	0.862	0.294	0.044	0.003	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.004	0.000	0.	0.	0.
6850.0	2.008	0.648	0.173	0.051	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.045	0.009	0.022	0.000	0.004
6860.0	4.247	1.355	0.477	0.236	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.142	0.136	0.100	0.010	0.034
6870.0	8.462	2.717	1.180	0.762	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.28[illegible]	0.339	0.354	0.061	0.110
6875.0	11.352	3.879	1.808	1.256	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.608	0.576	0.544	0.086	0.181
6880.0	13.277	5.449	2.680	1.899	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.932	0.870	0.829	0.159	0.283
6885.0	15.443	7.444	3.836	2.773	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.376	1.262	1.186	0.272	0.420
6890.0	24.014	9.986	5.370	3.962	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.977	1.776	1.636	0.417	0.623
6895.0	28.777	13.007	7.317	5.416	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	2.762	2.504	2.163	0.600	0.886
8898.7	32.364	15.362	9.073	6.713	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	3.453	3.033	2.597	0.749	1.128
6902.3	35.967	18.313	11.064	8.210	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	4.312	3.565	3.004	0.915	1.416
8905.8	39.461	21.321	13.[illegible]2	9.660	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	5.360	4.314	3.493	1.132	1.769
8909.3	42.961	24.311	16.000	11.920	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	6.343	5.123	4.334	1.370	2.175
6912.6	46.241	27.454	18.716	14.105	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	7.930	6.193	5.133	1.688	2.684
8913.9	49.561	30.867	21.610	16.506	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	9.697	7.246	6.036	1.989	3.256
6919.2	52.641	34.093	24.338	18.954	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	11.116	8.346	6.912	2.312	3.886
6922.3	55.961	37.149	27.410	21.338	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	12.757	9.459	7.765	2.617	4.476
6925.4	59.041	40.218	30.297	23.786	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	14.443	10.585	8.641	2.924	5.107
6928.4	62.041	43.193	33.119	26.205	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	16.132	11.731	9.508	3.234	5.741
6930.9	64.541	45.695	35.496	28.246	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	17.537	12.726	10.276	3.526	6.305
6934.2	67.841	48.954	38.612	30.888	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	19.275	13.928	11.264	3.885	6.928
6937.0	70.641	51.738	41.283	33.144	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.838	15.042	12.172	4.216	7.518
6939.7	73.341	54.433	43.931	35.473	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	22.619	16.268	13.135	4.578	8.214
6942.4	76.041	57.133	46.616	38.003	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	24.380	17.732	14.269	5.020	9.099
6944.9	78.541	59.633	49.112	40.445	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	26.799	19.286	15.484	5.507	10.091
6947.5	81.141	62.233	51.712	43.022	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	29.112	21.062	16.908	6.088	11.248
6949.9	83.341	64.633	54.112	45.418	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	31.338	22.885	18.406	6.717	12.445
6952.2	85.841	66 933	56.612	47.684	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	33.266	24.416	19.700	7.329	13.493
6954.5	88.141	69.233	58.712	49.888	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	34.991	23.564	20.553	7.613	14.146
6956.7	90.341	71.433	60.912	52.020	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	36.691	26.076	21.363	7.902	14.806
6958.8	92.441	73.533	63.012	54.069	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	38.344	27.791	22.184	8.185	15.472
6960.9	94.341	75.633	65.112	56.127	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	40.064	28.821	23.023	8.473	16.157
6962.9	96.341	77.633	67.112	58.093	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	41.697	30.005	23.840	8.750	16.822
6964.8	98.441	79.333	69.[illegible]2	59.938	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	43.241	31.022	24.591	9.013	17.452
6966.6	100.241	81.333	70.8[illegible]	61.719	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	44.684	31.976	25.304	9.233	18.027
6968.4	102.041	83.133	72.612	63.460	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	46.068	32.877	25.975	9.478	18.560
6970.1	103.741	84.833	74.311	65.064	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	47.280	33.656	26.550	9.666	19.016
6972.5	106.141	87.228	76.698	66.998	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	48.316	34.416	27.138	9.840	19.433
6974.0	107.641	88.722	78.102	68.176	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	49.219	34.821	27.462	9.934	19.650
6975.4	109.041	90.122	79.492	69.471	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	50.161	35.469	27.815	10.063	19.995
6976.8	110.441	91.522	80.890	70.846	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	51.295	36.157	28.376	10.286	20.496
6978.1	111.741	92.822	82.190	72.138	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	52.435	36.978	29.005	10.513	20.972
6979.3	112.941	94.022	83.390	73.338	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	53.578	37.822	29.638	10.733	21.321
6982.0	115.641	96.722	86.090	76.036	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	56.203	39.979	31.364	11.428	22.987
6984.3	117.641	98.722	88.090	78.039	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	58.182	41.748	32.844	12.039	24.266
6986.0	119.641	100.722	90.090	80.038	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	60.187	43.615	34.491	12.781	25.716
6988.0	121.641	102.722	92.090	82.038	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	62.150	45.550	36.298	13.766	27.381
6990.0	123.441	104.712	94.058	83.800	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	63.982	46.724	37.426	14.339	28.351
6992.0	125.634	106.383	95.410	84.393	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	63.515	46.808	37.495	14.350	28.372
6994.3	127.923	107.461	96.099	84.839	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	63.568	46.843	37.514	14.353	28.378
6996.0	129.170	108.221	96.528	84.982	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	63.598	46.864	37.528	14.354	28.380
6998.0	130.562	108.770	96.833	85.078	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	63.616	46.880	37.538	14.356	28.380
7000.0	131.730	109.203	97.066	85.153	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	63.630	46.892	37.544	14.356	28.380
7005.0	134.037	109.971	97.479	83.284	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	63.633	46.898	37.547	14.356	28.380
7010.0	135.710	110.480	97.738	85.332	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	63.636	46.898	37.547	14.356	28.380
7015.0	136.956	110.856	97.919	85.388	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	63.636	46.898	37.547	14.356	28.380
7020.0	137.908	111.147	98.056	85.417	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	63.636	46.898	37.547	14.356	28.380
7030.0	139.395	111.585	98.250	85.456	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]					
7040.0	140.381	111.911	98.389	85.467	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]					
7050.0	141.097	112.165	98.516	85.467	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]					
7060.0	141.733	112.399	98.611	85.467	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]					
7100.0	142.753	112.691	98.660	85.467	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]					
7127.0	143.239	112.752	98.880	85.467														

Table 6-2 $\left[\int_{\nu} A(\nu)d\nu\right]$ (continued)

Sam. No.	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38
p(atm)	7.70_{-2} x 10^{-2}	2.00_{0} x 10^{0}	2.00_{0} x 10^{0}	2.34_{-2} x 10^{-2}	2.34_{-2} x 10^{-2}	2.34_{-2} x 10^{-2}	1.18_{-2} x 10^{-2}	1.00 x 10^{0}	6.66 x 10^{-1}	2.17 x 10^{-1}	6.66 x 10^{-1}	2.17 x 10^{-1}	2.17_{-1} x 10^{-1}	7.63_{-3} x 10^{-3}	7.63 x 10^{-3}	8.00_{0} x 10^{0}	2.02_{0} x 10^{0}
P (atm)	7.70_{-2} x 10^{-2}	2.00_{0} x 10^{0}	2.00_{0} x 10^{0}	2.03_{-1} x 10^{-1}	8.47_{-2} x 10^{-2}	2.36_{-2} x 10^{-2}	1.18 x 10^{-2}	1.46 x 10^{1}	1.29 x 10^{1}	1.29 x 10^{1}	6.66 x 10^{-1}	9.34 x 10^{-1}	2.17_{-1} x 10^{-1}	2.76 x 10^{-2}	7.63_{-3} x 10^{-3}	8.00_{0} x 10^{0}	2.02_{0} x 10^{0}
u(atm cm) STP	3.32_{3} x 10^{3}	6.40_{3} x 10^{3}	1.53_{3} x 10^{3}	1.01_{3} x 10^{3}	1.01_{3} x 10^{3}	1.01_{3} x 10^{3}	1.01_{3} x 10^{3}	3.86 x 10^{2}	1.01_{3} x 10^{3}	3.30 x 10^{2}	1.01 x 10^{3}	3.30 x 10^{2}	3.30_{2} x 10^{2}	3.28 x 10^{2}	3.29_{2} x 10^{2}	2.17_{3} x 10^{3}	1.05_{3} x 10^{3}
ν (cm^{-1})	ν=6820 cm^{-1}	ν=6820 cm^{-1}	ν=6820 cm^{-1}	ν=6855 cm^{-1}	ν=6855 cm^{-1}	ν=6855 cm^{-1}	ν=6855 cm^{-1}	ν=6870 cm^{-1}	ν=6870 cm^{-1}	ν=6870 cm^{-1}	ν=6870 cm^{-1}	ν=6870 cm^{-1}	ν=6870 cm^{-1}	ν=6870 cm^{-1}	ν=6870 cm^{-1}	ν=6820 cm^{-1}	ν=6820 cm^{-1}
[illegible]	0.	0.	0.													0.027	0.000
[illegible]	0.	0.006	0.													0.709	0.030
[illegible]	0.	0.064	0.005													0.278	0.114
[illegible]	0.064	0.185	0.037	0.067	0.	0.	0.									0.555	0.254
[illegible]	0.071	0.366	0.098	0.045	0.011	0.001	0.	0.	0.							1.021	0.469
[illegible]	0.135	0.562	0.141	0.077	0.028	0.018	0.001	0.	0.006	0.						1.383	0.645
[illegible]	0.206	0.732	0.193	0.125	0.052	0.028	0.012	0.	0.031	0.006						1.851	0.871
[illegible]	0.362	1.023	0.265	0.204	0.085	0.059	0.039	0.000	0.065	0.003						2.399	1.148
[illegible]	0.543	1.432	0.367	0.302	0.146	0.117	0.080	0.005	0.126	0.011						3.046	1.487
[illegible]	0.761	1.974	0.511	0.429	0.226	0.194	0.149	0.010	0.222	0.033						3.798	1.834
[illegible]	0.774	2.496	0.647	0.533	0.297	0.260	0.203	0.020	0.304	0.056						4.313	2.145
[illegible]	1.160	3.124	0.812	0.654	0.379	0.334	0.268	0.026	0.414	0.082						5.070	2.494
[illegible]	1.497	3.923	1.030	0.806	0.479	0.431	0.349	0.133	0.556	0.110						5.582	2.921
[illegible]	1.734	4.900	1.313	0.974	0.605	0.562	0.446	0.196	0.743	0.166						6.895	3.446
[illegible]	2.100	6.058	1.661	1.140	0.764	0.678	0.561	0.272	0.972	0.233						..045	4.059
[illegible]	2.469	7.367	2.072	1.424	0.943	0.825	0.689	0.368	1.247	0.324						9.804	4.776
[illegible]	2.477	8.819	2.536	1.703	1.143	0.981	0.828	0.482	1.582	0.447						10.574	5.427
[illegible]	3.305	10.305	3.043	1.997	1.332	1.120	0.951	0.619	1.944	0.569						11.793	6.109
[illegible]	3.703	11.464	3.600	2.268	1.552	1.261	1.041	0.757	2.344	0.701						12.894	6.781
[illegible]	4.143	13.476	4.199	2.572	1.742	1.405	1.197	0.921	2.781	0.845	2.442	0.799	0.696	0.674	0.694	14.295	7.617
[illegible]	4.523	14.693	4.764	2.832	1.953	1.540	1.510	1.076	3.189	0.989	2.768	0.928	0.800	0.746	0.757	15.295	8.186
[illegible]	4.903	16.659	5.462	3.129	2.158	1.886	1.442	1.307	3.785	1.194	3.180	1.097	0.928	0.823	0.822	16.610	8.987
[illegible]	5.323	18.323	6.207	3.419	2.328	1.822	1.532	1.562	4.339	1.407	3.573	1.267	1.049	0.891	0.875	17.858	9.210
[illegible]	5.473	20.166	7.074	3.772	2.557	1.985	1.685	1.827	5.131	1.608	4.048	1.479	1.206	0.969	0.942	19.264	9.967
[illegible]	6.447	22.276	8.115	4.204	2.856	2.188	1.845	2.180	6.042	2.302	4.645	1.750	1.400	1.073	1.030	20.909	10.824
[illegible]	7.111	24.421	9.277	4.708	3.218	2.431	2.038	2.614	7.057	2.383	5.315	2.064	1.634	1.202	1.134	22.621	11.714
[illegible]	7.873	26.765	10.615	5.308	3.635	2.723	2.272	3.135	8.259	2.650	6.122	2.451	1.918	1.357	1.266	24.581	12.682
[illegible]	8.574	29.049	11.970	5.915	4.072	5.037	2.533	3.679	9.69	3.332	6.931	2.847	2.209	1.519	1.411	26.643	14.259
[illegible]	9.494	31.47	13.[illegible]	6.496	4.508	5.352	2.798	4.216	10.629	3.793	7.675	3.222	2.467	1.665	1.533	28.454	15.981
[illegible]	[illegible]	34.[illegible]	16.411	6.859	4.727	3.479	2.886	4.713	11.737	4.232	8.286	3.561	2.662	1.736	1.587	30.955	16.363
[illegible]	10.[illegible]	36.467	17.[illegible]	7.242	4.950	3.607	2.975	5.212	12.641	4.575	8.902	3.848	2.864	1.807	1.642	31.360	17.076
[illegible]	10.[illegible]	36.428	17.706	7.611	5.164	3.735	3.057	5.459	13.020	4.710	9.413	4.195	3.066	1.877	1.692	32.711	17.782
[illegible]	11.[illegible]	39.735	17.917	7.991	5.581	3.884	3.146	6.211	15.004	5.545	10.149	4.344	3.281	1.948	1.742	34.196	18.515
[illegible]	11.[illegible]	40.944	19.936	8.355	5.595	3.987	3.227	6.679	16.017	5.950	10.750	4.870	3.477	2.013	1.791	35.296	19.143
[illegible]	11.461	42.269	20.783	8.763	5.799	4.105	3.305	7.102	16.931	6.309	11.315	5.166	3.662	2.081	1.836	36.417	19.728
[illegible]	12.[illegible]	43.468	21.[illegible]	9.022	5.991	4.214	3.373	7.462	17.721	6.610	11.840	5.428	3.831	2.144	1.882	37.494	20.263
[illegible]	12.582	44.427	21.912	9.321	6.161	4.316	3.442	7.769	18.402	6.860	12.322	5.659	3.985	2.202	1.921	38.537	20.697
[illegible]	12.[illegible]	46.[illegible]	22.612	9.579	6.513	4.404	3.498	8.063	18.925	7.065	12.716	5.831	4.111	2.250	1.957	39.416	21.019
[illegible]	13.077	46.323	23.241	9.812	6.441	4.483	3.558	8.241	19.461	7.230	13.075	5.970	4.210	2.296	1.994	39.539	21.250
[illegible]	13.[illegible]	49.134	23.517	9.965	6.513	4.521	3.586	8.371	19.737	7.344	13.[illegible]	6.017	4.250	2.317	2.010	39.917	...580
[illegible]	13.[illegible]	50.136	23.993	10.073	6.624	4.600	3.631	8.534	20.139	7.496	13.439	..116	4.336	2.359	2.036	40.487	21.641
[illegible]	13.737	51.435	24.674	10.316	6.772	4.691	3.654	8.775	20.663	7.726	13.824	6.289	4.446	2.411	2.073	41.214	22.039
[illegible]	14.[illegible]	52.673	25.473	10.594	6.942	4.789	3.756	9.079	21.550	8.006	14.[illegible]	6.519	4.622	2.469	2.112	42.660	22.498
[illegible]	14.446	53.887	26.316	10.889	7.126	4.897	3.829	9.420	22.311	8.332	14	6.775	4.792	2.532	2.152	42.952	23.018
[illegible]	15.434	56.535	28.493	11.739	7.844	5.196	4.033	10.471	24.320	9.296	16.127	7.538	5.271	2.712	2.268	45.228	24.502
[illegible]	16.[illegible]	58.827	30.263	12.503	8.118	5.468	4.225	11.[illegible]	25.974	10.169	17.311	8.235	5.709	2.870	2.375	47.068	25.457
[illegible]	17.[illegible]	6..925	32.116	13.[illegible]	8.685	5.808	4.470	12.[illegible]	27.697	11.121	18.643	9.043	6.229	3.065	2.509	48.946	27.392
[illegible]	18.[illegible]	62.916	34.[illegible]	14.969	9.443	6.308	4.837	13.544	29.437	12.121	20.147	9.972	6.895	3.360	2.725	50.909	29.131
[illegible]	19.[illegible]	64.355	35.243	15.361	9.957	6.645	5.147	14.[illegible]	30.366	12.593	21.285	10.617	7.370	3.605	2.923	52.556	30.457
[illegible]	13.227	64.349	35.396	15.375	9.961	6.648	5.149	14.362	30.491	12.634	21.336	10.635	..378	3.609	2.924	52.936	30.517
[illegible]	14.[illegible]	64.563	35.430	15.377	9.961	6.648	5.149	14.369	30.539	12.644	21.343	10.641	7.379	3.609	2.924	53.060	30.533
[illegible]	14.239	64.[illegible]	35.450					14.[illegible]	30.568	12.649	21.350	10.645	7.379	3.60[illegible]	2.924	53.131	30.542
[illegible]	19.[illegible]	..4.686	35.460					14.[illegible]	30.[illegible]	12.652	21.353	10.645	7.379	3.609	2.924	53.182	30.549
[illegible]	19.[illegible]	64.730	35.467					14.378	30.639	12.654	21.353	10.645	7.379	3.609	2.924	53.219	30.553
[illegible]	14.[illegible]	64.813	35.479					14.387	30.609	12.655						53.277	30.554
[illegible]	14.[illegible]	64.877	35.48[illegible]													53.316	30.554
[illegible]	14.[illegible]	64.912	35.48[illegible]													53.338	30.554
[illegible]	14.[illegible]	64.[illegible]	[illegible]													53.366	30.554
[illegible]	14.[illegible]	64.[illegible]	35.48[illegible]													53.383	30.554
[illegible]	14.[illegible]	64.[illegible]	35.48[illegible]														

SECTION 7

REFERENCES

1. C. P. Courtoy, Annales de la Societe Scientifique de Bruxelles, Serie 1, pp 5-230 (27 March 1959). Also, C. P. Courtoy, Canad. J. Phys. 35, 608 (1957).
2. J. N. Howard, D. E. Burch and Dudley Williams, J. Opt. Soc. Am. 46, 237 (1956).
3. G. P. Kuiper, Communications of Lunar and Planetary Laboratory, Vol. 1, No. 14-16, University of Arizona Press (1962).
4. D. E. Burch, D. A. Gryvnak and R. R. Patty, Absorption of CO_2 Between 4500 and 5400 cm^{-1}, Aeronutronic Report U-2955, Contract NOnr 3560(00), (15 December 1964).
5. D. E. Burch, D. A. Gryvnak and Dudley Williams, Appl. Opt. 1, 759 (1962).
6. D. E. Burch, D. A. Gryvnak, R. R. Patty and Charlotte Bartky, The Shapes of Collision-Broadened CO_2 Absorption Lines, Aeronutronic Report (to be published), Contract NOnr 3560(00).
7. V. R. Stull, P. J. Wyatt and G. N. Plass, The Infrared Absorption of Carbon Dioxide, Aeronutronic Report U-1505, Contract AF19(604)-7479, (30 December 1961).
8. G. N. Plass, J. Opt. Soc. Am. 48, 690 (1958).
9. G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand Co. (See 266ff for a discussion of the intensities of difference bands) (Ninth Printing 1960).
10. B. H. Winters, S. Silverman and W. S. Benedict, J. Quan. Spec. 4, 527 (1964).
11. R. Ladenberg and F. Reiche, Ann. Physik 42, 181 (1913).
12. R. P. Madden, J. Chem. Phys. 35, No. 6, 2083 (1961).
13. R. M. Goody, Atmospheric Radiation, Oxford University Press, (1964).
14. O. C. Mohler, A Table of Solar Spectrum Wavelengths 11984A to 25578A, University of Michigan Press, (1955)